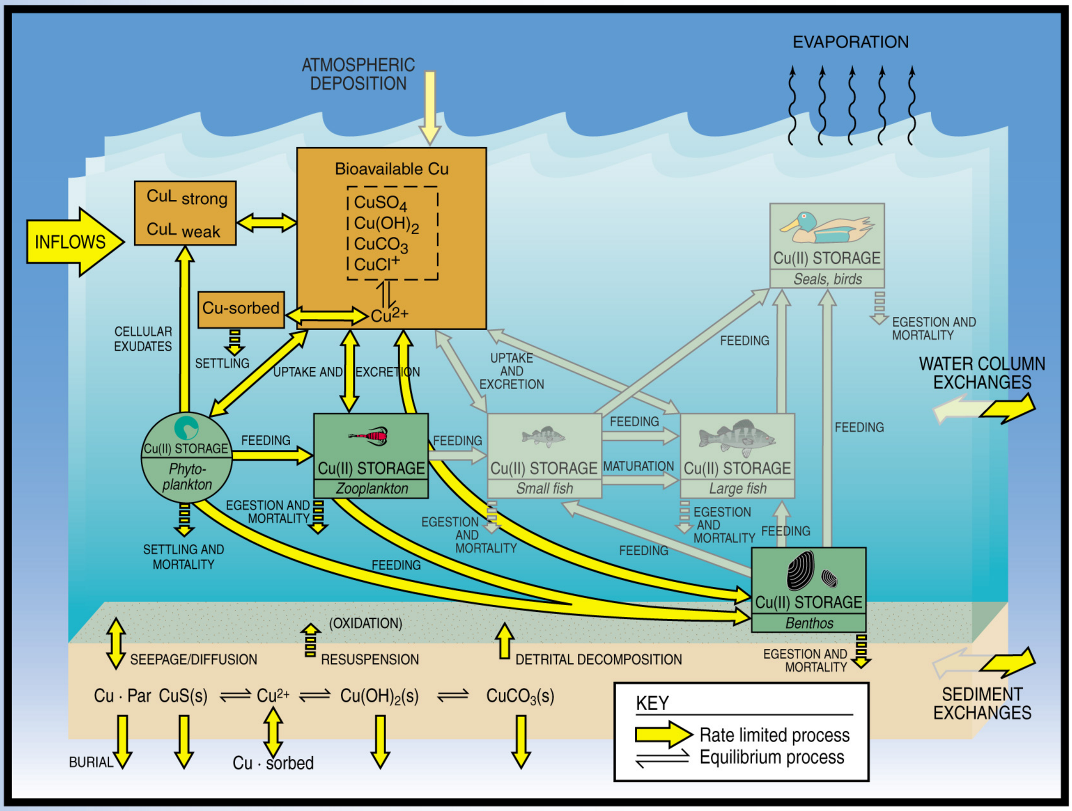
TASK 1
CONCEPTUAL MODEL REPORT FOR COPPER AND NICKEL IN LOWER SOUTH SAN FRANCISCO BAY



Final Report

December 1999

Prepared by Tetra Tech, Inc.

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Acknowledgements

The Conceptual Model for Copper and Nickel in Lower South San Francisco Bay is the product of co-operative efforts by several groups. Funding was provided by the City of San Jose's Environmental Services Department. Guidance for the development of the conceptual model was provided by the TMDL Work Group (TWG). This group was formed by the Santa Clara Basin Watershed Management Initiative, and participants include representatives from regulatory agencies, environmental advocacy groups, industry, and municipalities. The TWG oversaw model development, reviewed draft reports, made recommendations on the required level of technical and graphic detail, and approved the final report. In the review process, a Technical Review Committee was formed to provide expert review of the conceptual model. Members of the Technical Review Committee were Dr. Sam Luoma from the U.S. Geological Survey, Dr. Janet Hering from California Institute of Technology, and Dr. Steven Monismith from Stanford University. Their recommendations were incorporated into this report. The conceptual model report was prepared by Tetra Tech, Inc.

This report was prepared under Task 1 of the project entitled: *Calculation of Total Maximum Daily Loads for Copper and Nickel in Lower South San Francisco Bay.* Two additional reports were produced under Task 2 of the project: Source Characterization Report and the Impairment Assessment Report. Together these three reports were used to assess the impairment of beneficial uses in the South Bay and the need to complete the TMDL.

The TWG believes that the conceptual model report provides an excellent summary of the existing knowledge on the behavior of copper and nickel in South San Francisco Bay and the factors that affect the cycling and potential toxicity of these metals in the ecosystem.

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CONCEPTUAL MODEL REPORT FOR COPPER AND NICKEL IN LOWER SOUTH SAN FRANCISCO BAY

Final Report

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TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

Figures appear at the end of each section

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EXECUTIVE SUMMARY

This report presents the conceptual model for copper and nickel that has been developed as a part of the Total Maximum Daily Loads (TMDL) project for Lower South San Francisco Bay. Existing data are analyzed to summarize the current understanding of copper and nickel cycling in Lower South San Francisco Bay. First, the loadings, mass balances, and inventories of copper and nickel are calculated. Next, the processes that are thought to be the most important in controlling copper and nickel cycling are described. Finally, the effects of copper and nickel cycling on the uptake and toxicity to aquatic organisms are discussed. This is followed by a series of recommendations for further studies.

By explicitly identifying the important processes that control copper and nickel cycling and summarizing our understanding of these processes, the conceptual model provides a technical basis for TMDL project planning. The information presented in this report will be used to guide the scope and direction of the other tasks, as well as the overall technical approach for the development of the TMDLs.

The key elements of the conceptual model are summarized in the following sections.

Copper and Nickel Concentrations

The average total copper concentration in the Lower South San Francisco Bay is 12.3 µg/l during the dry season and 10.7 µg/l during the wet season. These are higher than the corresponding values in the Central South Bay, which are 3.2 µg/l and 2.1 µg/l, respectively, and much higher than the corresponding values in the ocean just west of the Golden Gate, which are 0.5 µg/l and 0.7 µg/l, respectively. The same general pattern of decreasing concentrations from the Lower South Bay toward the ocean is found with the average dissolved copper. During the dry season, the dissolved copper concentration is 3.3 µg/l in the Lower South Bay, 2.2 µg/l in the Central South Bay, and 0.4 µg/l west of the Golden Gate. During the wet season, the dissolved copper concentration is 2.4 µg/l in the Lower South Bay, 1.6 µg/l in the Central South Bay, and 0.5 µg/l west of the Golden Gate.

The average total nickel concentration in the Lower South San Francisco Bay is 23.8 µg/l during the dry season and 20.6 µg/l during the wet season. These are higher than the corresponding values in the Central South Bay, which are 2.5 µg/l during both seasons, and much higher than the corresponding values in the ocean just west of the Golden Gate, which are 0.6 µg/l and 0.9 µg/l, respectively. The same general pattern is found with the average dissolved concentrations of nickel. During the dry season, the dissolved nickel concentration is 3.8 µg/l in the Lower South Bay, 1.6 µg/l in the Central South Bay, and 0.5 µg/l west of the Golden Gate. During the wet season, the dissolved nickel concentration is 2.9 µg/l in the Lower South Bay, 1.6 µg/l in the Central South Bay, and 0.71 µg/l west of the Golden Gate. These patterns indicate enrichment of copper and nickel in the Lower South Bay.

The copper concentration in surficial sediments in the Lower South Bay is about 40 mg/kg. Similar concentrations have been measured to the north of the Dumbarton Bridge. Background sediment concentrations are about 25 mg/kg, based on a deep core near the San Mateo Bridge.

Sediments from Tomales Bay have copper concentrations of about 20 mg/kg, similar to the South Bay background value, but about half the concentration of the Lower South Bay surficial sediments.

Nickel concentrations in Lower South Bay surficial sediments average 99 mg/kg during the dry season and 109 mg/kg during the wet season. These values are only slightly higher than estimated background concentrations of 90 mg/kg based on a deep core near the San Mateo Bridge. However, nickel concentrations in Tomales Bay sediments are higher than in the Lower South Bay, ranging from 100 to 130 mg/kg.

Copper and Nickel Loadings

The two largest sources of total copper and nickel to the Lower South San Francisco Bay are sediment exchange during resuspension and nonpoint source loads from tributaries. Most of the tributary loads occur during the wet season. Resuspension is highest during the windy spring and summer months, but also occurs during the rest of the year during periods of high winds or currents. During the dry season, the relative contributions of the POTW loads are higher than during the wet season since tributary nonpoint source loads become small.

Point sources are major contributors of dissolved copper and nickel, since nonpoint sources are believed to contribute primarily particulate loads. Internal cycling processes are also important components of the dissolved copper and nickel loads, particularly during the dry season. Mass balance calculations presented in Appendix B show that during the dry season, internal cycling fluxes occur that are similar in magnitude to the dissolved copper and nickel fluxes from the POTW discharges. These are the two largest sources of dissolved metals to the water column during this season. The specific processes causing the internal cycling fluxes cannot be identified with the available data, but they could include net desorption of metals during sediment resuspension, decomposition of algal detritus in the sediment, and solubilization of metals in phytoplankton during feeding by benthic bivalves. During the wet season, the mass balance calculations indicate that internal cycling processes result in a net sink of dissolved copper and nickel from the water. Again, the specific processes cannot be identified with the available data, but they could include net adsorption of metals on suspended solids entering the South Bay from tributary inflows and uptake by phytoplankton during the spring blooms. The magnitudes of the internal cycling fluxes are similar during both seasons, but they represent a dissolved source during the dry season and a dissolved sink during the wet season. The estimated cycling fluxes have high uncertainties due to the existing data limitations and simplifying assumptions required in the analyses.

Copper and nickel loads from sediment diffusion and atmospheric deposition appear to be relatively small, and together represent only a few percent of the total loads.

Sediment Transport Processes

Sediment transport is very important to the cycling of copper and nickel, since sediment resuspension is one of the largest sources of the metals. The particle size distribution of suspended sediments is smaller than the particle size distribution of sediments in the bed. This affects the fate and transport of the adsorbed metals, since they associate more strongly and therefore have higher concentrations on the smaller particles. A fraction of the sediments that erode from the watershed appear to be deposited in streambeds in the flatlands, and may enter the South Bay during subsequent storm events. Wetting and drying of the sediment bed is a prominent feature of the Lower South Bay that influences sediment transport.

Copper and Nickel Cycling

Copper and nickel cycling is important in Lower South San Francisco Bay because it plays a major role in both the fate and toxicity of the metal loads entering the estuary. The conceptual model of cycling involves chemical speciation of the metals and the chemical, physical, and biological processes that influence their fate, concentrations, and interactions between chemical forms. The species considered are the free metal ions; inorganic complexes with chlorides, hydroxides, carbonates, and sulfates; organic complexes with strong and weak ligands; and adsorbed forms and other particulate forms. Speciation is very important since only free metal ions and labile inorganic complexes are bioavailable for uptake. Therefore, these are also the forms that determine toxicity.

However, only a small fraction of the total copper and nickel in the water column occurs in these forms. Much of the dissolved copper and nickel is complexed with organic ligands, and particulate forms also represent a significant fraction of the total metal concentrations. The free ions and inorganic complexes have been estimated to range from 8 to 20 % of the total dissolved copper and 50 to 66 % of the total dissolved nickel in South San Francisco Bay (Donat et al., 1994). However, this distribution could change as metal loads or ligand loads to the estuary change, or if other changes occur in the Bay that affect the internal cycling of the metals. Therefore, it is important to understand the processes that control the transformations between different chemical forms of the metals, since these will determine the speciation and concentrations of the metals as loads or internal cycling processes change in the future.

Speciation Processes

Complexation and adsorption are the main processes that control copper and nickel speciation. Inorganic complexation reactions are fast, and can be considered as equilibrium processes. Seasonal salinity variations have the largest effect on these reactions, since that determines the concentrations of the inorganic ligands that complex with the metals. Organic complexation and sorption reactions are slower, and are considered to be kinetically limited. These slow kinetics make the organic complexes and sorbed species unavailable for uptake, as well as influencing their fate and transport in the estuary.

Adsorption processes are believed to depend on free metal ion concentrations. Organic complexation reactions depend on the relative concentrations of organic ligands and dissolved metals. Two major classes of organic ligands have been identified in the South Bay, weaker ligands such as humic substances, and very strong ligands such as synthetic chelating agents (Donat et al., 1994; Sedlak et al., 1997; Bedsworth and Sedlak, 1999). Bedsworth and Sedlak (1999) have identified EDTA as the major strong ligand for nickel in the South Bay, and have identified the source to be wastewater effluents. Almost all of the organically complexed nickel in the South Bay is associated with this strong ligand, while the weaker ligand class contains a major portion of the complexed copper (Donat et al., 1994; Bedsworth and Sedlak, 1999). The slow dissociation rates of these strong organic complexes may prevent speciation changes before the metals are transported out of the Lower South Bay.

Sediment Cycling Processes

Sediment processes are also important in the speciation and cycling of copper and nickel. The redox conditions are lower in the sediments, producing different chemical reactions than occur in the water column. Soluble fluxes between the water column and sediments are low compared to other sources of the metals. However, sediment resuspension and desorption may release large quantities of dissolved copper and nickel to the water column, making this a major source of dissolved metals.

Biological Cycling

The biological portion of the conceptual model includes the effects of organisms on the cycling of copper and nickel in the water and sediments, and the accumulation of the metals in the food web. Organisms influence biogeochemical cycling through uptake and excretion processes, incorporation into biological tissues, production of organic detrital material containing the metals, and subsequent metals release during decomposition and mineralization. Uptake removes dissolved metals from the water column and incorporates them in the biota, while excretion returns metals back to the water in soluble forms. However, this biological processing can change the form and bioavailability of the metals. Free metal ions and weak inorganic complexes are the forms that are most readily assimilated from the water, while excreted forms may be complexed with organic ligands that are much less available for uptake. In addition, phytoplankton excrete cellular exudates that chelate copper ions, effectively reducing copper bioavailability and toxicity.

Particulate organic detrital copper and nickel are produced through food web processing. Following accumulation of the metals in the biota, processes such as phytoplankton settling, plankton mortality, and egestion generate organic detrital metals that settle and deposit the metals in the sediments. These metals are released as soluble forms to the water column and sediment porewaters as the organic material decomposes. Solubilization of the metals by benthic animals feeding on phytoplankton and detritus could also be an important process, as could benthic bioturbation/irrigation effects on sediment release.

Phytoplankton Uptake and Removal Fluxes

The most important biological component of the copper and nickel biogeochemical cycles is processing by the phytoplankton. In order to assess the importance of biological cycling, phytoplankton uptake removal fluxes were estimated and compared with the loads. Since phytoplankton metal concentrations are not available for the South Bay, they were estimated from uptake experiments in the literature using the free ion concentrations of copper and nickel in the South Bay. These values were used in conjunction with estimates of phytoplankton growth and productivity to estimate the metal uptake fluxes. Although there is some uncertainty in these estimates, the results indicate that phytoplankton processing is the same order of magnitude as current POTW loads into the Lower South Bay. Although, significant copper depletion was not observed during a phytoplankton bloom in the South Bay, nickel and other metals were removed (Luoma et al., 1998). The algal fluxes could have been obscured by higher resuspension or wet season runoff fluxes which exceeded algal uptake during the bloom.

Phytoplankton Uptake and Toxicity

Phytoplankton uptake and toxicity from copper and nickel are extremely important in Lower South San Francisco Bay, since phytoplankton are among the most sensitive organisms to copper toxicity, and since phytoplankton form the base of the food web. Phytoplankton accumulation of metals is the major route of entry into the rest of the food web, and phytoplankton uptake also influences the biogeochemical cycling of the metals.

Copper and nickel are taken up by nutrient metal transport proteins on the phytoplankton cell membranes. Since phytoplankton have specific nutrient requirements, they have cellular feedback mechanisms which allow them to regulate intracellular metal concentrations to levels that are optimum for growth and metabolism. Only free metal ions and labile inorganic metal complexes are available for uptake since metals complexed to strong organic ligands or adsorbed to suspended particles cannot cross the cell membrane. Water quality factors such as pH, alkalinity, hardness, dissolved organic matter, and suspended particulates influence the speciation and therefore uptake of the metals. Competition with other metals can inhibit both copper and nickel uptake, as well as the uptake of other nutrient metals. This occurs through both competition for uptake sites on the cell membrane, as well as through intracellular sites that control membrane transport rates of the metals.

Toxic effects on phytoplankton are typically measured in terms of reductions in growth rates. Therefore, toxicity can be produced both by nutritional deficiencies in competing nutrient metals, and by the accumulation of excess toxic metals, which disrupt the normal metabolism of the cell. Phytoplankton have three ways of reducing toxicity when exposed to excessive concentrations of copper and nickel: production of phytochelatin which binds the metals inside the cells and stores them in a nontoxic form, excretion of organic cellular exudates which chelate copper ions and reduce bioavailability, and induction of efflux systems to excrete accumulated metals from the cells.

Food Web Accumulation

Accumulation of copper and nickel in the aquatic food web depends on uptake from two routes of exposure, water and food. Accumulation can be calculated from the metal uptake rates from water; metal assimilation efficiencies from food; metal elimination rates from the organisms; organism growth rates, consumption rates, and dietary preferences; and metal concentrations in food items. The uptake and elimination rates must consider the effects of metal regulation by the organisms, at least for copper. A steady-state approach can be used to estimate total metal concentrations in different organisms and relative contributions from water and food. Alternatively, a dynamic food web model can be constructed to predict metal concentrations throughout the food web in response to changing exposure conditions, for example, from seasonal variations in the loading and cycling of the metals, or to future projected conditions in the South Bay. Currently, copper and nickel measurements in aquatic organisms in Lower South San Francisco Bay are limited to benthic bivalves.

Uncertainties

Several major sources of uncertainty were identified during the development of the conceptual model due to limitations in the currently available data for several key loading sources and processes. Little information is available on the sedimentation/resuspension dynamics in the Lower South San Francisco Bay and on the rate constants for the adsorption and desorption reactions for copper and nickel. This information is necessary to determine suspended sediment release fluxes of the metals, and the accumulation and release of the metals from the sediments. Very few sediment cores are available to estimate copper and nickel concentrations in sediment particles and porewaters. Nonpoint source tributary loads are not regularly monitored, so load estimates are based on simulation model predictions that have major uncertainties due to both data limitations and model simplifying assumptions. Limited information is available on the speciation of copper and nickel in bay waters and major load sources. Speciation has only been measured on a few occasions, so knowledge of temporal variations in speciation and of the sources, cycling, and fate of organic ligands that control speciation is limited. Very little direct information is available on biological cycling and food web transfer processes since copper and nickel have only been measured in bivalves, not in phytoplankton, zooplankton, and fish. Much less information is available in the literature on the cycling, uptake, and toxicity of nickel than of copper. Less information is available on the wet season cycling and transport processes in the South Bay than for the dry season.

Recommendations for Further Studies

Several processes have been identified that would be important to the development of the TMDLs for copper and nickel, but for which there is either a lack of sufficient information or a high degree of uncertainty. These processes should be the focus of future studies. The highest priority should be to quantify the speciation of copper and nickel and the cycling processes that influence speciation, since this determines bioavailability, uptake, and toxicity to aquatic organisms. If it is determined that the potential exists for the impairment of beneficial uses due to copper or nickel concentrations in Lower South San Francisco Bay, then steps should be taken to better quantify the sources of these metals. Four key areas have been identified for future studies: 1) biogeochemical processes influencing chemical speciation, 2) effects of speciation and competing metals on phytoplankton uptake and toxicity, 3) resuspension fluxes and other sediment-water interactions, and 4) wet season tributary loads.

Technical Review

A Technical Review Committee (TRC) was convened on April 23, 1999 to review the draft report (April 1999). The committee members were Dr. Janet Hering from California Institute of Technology, Dr. Sam Luoma from U.S. Geological Survey, and Dr. Stephen Monismith from Stanford University. The final report was revised to incorporate the major suggestions of the reviewers. This included: 1) the copper and nickel concentrations and loading fluxes from different sources were presented separately for the wet and dry seasons, and ranges were given as well as average values; 2) the major uncertainties and data limitations concerning the loading estimates and internal cycling processes were identified and discussed in more detail; 3) the recommendations for additional studies were expanded to include the recommendations from the reviewers; and 4) the discussions of bioavailability and biological cycling were revised to reflect the reviewer comments.

1 INTRODUCTION

This report presents the conceptual model for copper and nickel that has been developed as a part of the Total Maximum Daily Loads (TMDL) project for Lower South San Francisco Bay. The Project Plan that was prepared for Task 1 (Tetra Tech, 1998a) describes three roles for the conceptual model: data synthesis, communication, and project planning.

Existing data are analyzed to summarize the current understanding of copper and nickel cycling in Lower South San Francisco Bay. First, the loadings, mass balances, and inventories of copper and nickel are calculated. Next, the processes that are thought to be the most important in controlling copper and nickel cycling are described. Finally, the effects of copper and nickel cycling on the uptake and toxicity to aquatic organisms are discussed.

This report makes extensive use of graphics to communicate the information that has been developed on copper and nickel cycling. The objective was to develop a tool for effectively communicating the existing information to a wide audience of interested stakeholders. It is intended that the diagrams presented in this document can be used to facilitate the discussions of upcoming TMDL issues, such as source characterization, beneficial-use impairment, simulation model development, and the design of special studies. Mathematical equations are used to a limited extent and are presented in the appendices.

By explicitly identifying the important processes that control copper and nickel cycling and summarizing our understanding of these processes, the conceptual model provides a technical basis for TMDL project planning. The information presented in this report will be used to guide the scope and direction of the other tasks, as well as the overall technical approach for the development of the TMDLs. During the project, the conceptual model will be updated as the understanding of copper and nickel cycling improves based on subsequent data collection, analysis, and suggestions by technical experts.

1.1 Components of Conceptual Model

The conceptual model consists of four interrelated model components. In each one, the uncertainties in the understanding of copper and nickel behavior in the Lower South San Francisco Bay are identified. Data gaps, information requirements, and opportunities to overcome these uncertainties are also identified. The four components are:

- **Copper and Nickel Sources to Lower South San Francisco Bay**. The sources include external loading from point sources, runoff from nonpoint sources, and atmospheric deposition, as well as internal sources such as exchange with contaminated sediments and exchange with Central San Francisco Bay waters.

- **Sediment Transport, Deposition, and Resuspension.** The significance of these processes to the fate of copper and nickel is discussed.

- **Copper and Nickel Cycling in the Water Column and Bedded Sediments**. These processes include: metal speciation; complexation; adsorption-desorption;

interactions with sediments, such as resuspension, porewater diffusion, and advection; sediment diagenesis, including oxidation-reduction reactions and metal precipitation; water column hydrodynamics; biological cycling processes; phytoplankton uptake and toxicity; and food web accumulation.

- **Forcing Functions**. These include tidal, meteorological, and hydrological factors.

1.2 Database and Geographic Information System

A database and geographic information system have been developed in conjunction with the conceptual model (Tetra Tech, 1998b) to facilitate the retrieval, display, analysis, and interpretation of the data. Specific categories of data in the database are:

- **Basemap Information**. Basemap information includes topographic and bathymetric information for San Francisco Bay and the surrounding areas, watershed and subwatershed boundaries, geologic information, surface water features, and highway/road systems.

- **Copper and Nickel Loading Data**. Loading information includes point and nonpoint source loadings within the South San Francisco Bay watershed, atmospheric deposition, exchange with bedded sediments, and exchange with water and sediments in Central San Francisco Bay.

- **Water Quality Monitoring Data**. These data consist of ambient copper and nickel concentrations in the water column, in bedded sediments, and in tissues of bivalves. Also included are numerous other water quality constituents such as nutrients, chlorophyll-a, and sediment quality constituents such as oxidation-reduction potential, grain size distribution, and hydrogen sulfide concentrations.

- **Hydrodynamic Data**. These data consist of constituents that have a direct effect on the movement of water throughout the Bay. They include salinity, water temperature, total suspended solids, and tidal information.

- **Hydrologic Data**. These data consist of the Delta inflow rates in North San Francisco Bay and flow rates of natural streams that discharge into South San Francisco Bay.

- **Meteorologic Data**. These data consist of precipitation, wind speed, air temperature, and evaporation.

1.3 Report Organization

Section 2 describes copper and nickel loadings, mass balances, and inventories of copper and nickel to Lower South San Francisco Bay. An overview of the conceptual model is also presented. Sections 3 through 5 describe the other three components of the conceptual model. Some of these descriptions are quite detailed and include supporting calculations in appendices. However, the major findings are summarized at the end of each section.

In Section 6, the database is used to provide specific information to help better understand spatial and temporal distributions of copper and nickel, and associated processes that influence those distributions. Without this information to balance the material presented in Sections 2 through 5, the discussions of the conceptual model components would be of a theoretical nature, and of reduced value. *Some readers may find that reading Section 6 first will help them achieve a better understanding of the material presented in Sections 2 through 5.*

Section 7 summarizes the major sources of uncertainty in the processes that are important to developing TMDLs for copper and nickel in the Lower South Bay, and presents recommendations for additional studies to reduce these uncertainties.

Appendices A, B, and C include calculations that support the information presented in Sections 2 and 4. These include speciation calculations, flux calculations for load sources and internal cycling processes, and sediment diffusion calculations. Appendix D presents a table summarizing the relative importance and uncertainties of various factors controlling the fate of copper and nickel in Lower South San Francisco Bay.

Appendix E presents a summary of the Technical Review Committee (TRC) review of the draft report (April 1999), along with the reviewer comments. The committee members were Dr. Janet Hering from California Institute of Technology, Dr. Sam Luoma from U.S. Geological Survey, and Dr. Stephen Monismith from Stanford University. The committee convened on April 23, 1999 to review the report. The final report was revised to incorporate the major suggestions of the reviewers. This included: 1) the copper and nickel concentrations and loading fluxes from different sources were presented separately for the wet and dry seasons, and ranges were given as well as average values; 2) the major uncertainties and data limitations concerning the loading estimates and internal cycling processes were identified and discussed in more detail; 3) the recommendations for additional studies were expanded to include the recommendations from the reviewers; and 4) the discussions of bioavailability and biological cycling were revised to reflect the reviewer comments.

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2 OVERVIEW OF CONCEPTUAL MODELS FOR COPPER AND NICKEL

An overview of the conceptual models for copper and nickel is described in Sections 2.2 and 2.3. Since there are many similarities in the two conceptual models, a more detailed description is first provided for copper. Then similarities and differences are presented for nickel without detailed discussion. First, however, copper and nickel concentrations, inventories, and loadings relevant to Lower South San Francisco Bay are discussed.

2.1 Loadings, Mass Balances, and Inventories of Copper and Nickel to Lower South San Francisco Bay

The calculation of loadings, mass balances, and inventories is the first step in identifying the important processes that affect the fate of copper and nickel in Lower South San Francisco Bay. The emphasis is primarily on differentiating large from small loadings. Additional information on the internal cycling of copper and nickel is presented subsequently in Section 4.

Figure 2-1 illustrates the important features of copper and nickel loading to South San Francisco Bay. Note that the spatial scale shown in the figure includes both Lower and Central South San Francisco Bay.

Figure 2-1 shows graphically the five primary source categories:

- Point sources
- Nonpoint sources associated with runoff and erosion
- Atmospheric deposition
- Exchange with the sediments
- Net exchange within the water column and bed load transport at the boundaries of the study area. (Alternative potential boundaries are shown in the figure to illustrate that the boundary for the study area has not been selected.)

The point sources are illustrated by discrete points to denote outfall locations. Atmospheric deposition is denoted by arrows with a single arrowhead located on the Bay waters. Nonpoint sources are denoted by the arrows that ring the study area. Bed exchange is denoted by short arrows with two arrowheads, located on the Bay waters. The exchange with Bay waters and sediments at the study area boundary is denoted by longer double-headed arrows. While Lower South San Francisco Bay is the primary area of concern for establishing TMDLs, from a technical standpoint the boundaries need to be located where boundary conditions can be prescribed for modeling purposes, and may not coincide with the boundaries of Lower South San Francisco Bay.

The graphs in Figure 2-1 illustrate the temporal variability and the cumulative loading that exist in each source of copper or nickel over an annual cycle. As shown in A and B of Figure 2-1, point sources are continuous throughout the year, but exhibit some seasonal variability, with slightly higher volumetric discharges occurring during the wet season. Nonpoint sources associated with runoff and erosion, on the other hand, are dominant during the rainy season. Thus, point source loads are likely to exceed nonpoint source loads for approximately six months of the year.

As shown in C and D of Figure 2-1, particulate exchange with the bed is depicted as being a large, continuous source of copper and nickel, while atmospheric deposition is insignificant in comparison. Over the course of a year, cumulative mass loadings from the two sources will differ significantly.

The existing information on concentrations, inventories, and loadings of copper and nickel to Lower South San Francisco Bay is summarized in Figures 2-2 to 2-5. The information used to generate the numbers in these figures came from the conceptual model database, from the Source Characterization Report (URS Greiner Woodward Clyde, 1998), and from modeling work performed by Stanford University (Monismith et al, 1999). Station locations mentioned in these figures are shown subsequently in Figure 6-1b for the three POTW releases, and in Figure 6-18b for the in-bay monitoring locations. The figures are subdivided into a six month dry season (June through November) and a six month wet season (December through May).

Copper concentration data are shown in Figure 2-2a (dry season) and Figure 2-2b (wet season). In the water column, concentrations are presented as both total and dissolved. To illustrate variability in the concentrations, ranges, as well as mean values, are shown. Concentration data are presented in Lower South San Francisco Bay, in South San Francisco Bay north of the Dumbarton Bridge, and near the mouth of San Francisco Bay. The data generally indicate the highest concentrations are in Lower South San Francisco Bay.

In the surficial sediments beneath the bay, the average copper concentration is 40 mg/kg and varies from about 25 mg/kg to 55 mg/kg. The approximate background concentration is 25 mg/kg, based on a sediment core taken near the San Mateo Bridge. Those results are shown subsequently in Figure 6-5b. An alternative estimate of background is 20 mg/kg, based on a core at Tomales Bay (shown in Figure 6-5b). To the north of the Dumbarton Bridge, surficial sediment copper concentrations are only slightly below those south of the Dumbarton Bridge.

Few soil copper data are presently available in the upland watershed to the South Bay. Copper concentrations of 34 mg/kg in Calabazas Creek sediments was reported in the Source Characterization Report (URS Greiner Woodward Clyde 1998). A range of copper concentrations (22-59 mg/kg) is shown in Figure 2-2 based on data recently received (Terry Cooke, personal communication, 1999)

The mass of copper in the water column and in the top meter of bedded sediments has been estimated and is shown in Figure 2-3. The water column inventories were calculated by multiplying the concentration by the mean-tide water volume. The mass in the sediments were obtained by multiplying the surficial copper concentration by the mass of sediments. The top 1 meter was used since the concentrations do not appear to vary considerably over depth. However, this is based on very limited data, such as shown in Figure 6-5b. Based on the copper concentration estimated above background, the "excess" mass of copper was calculated to be 0.6 to 0.7 $\cdot 10^6$ kg above background.

Fluxes, or loading, of copper from the atmosphere (120 kg/yr), from POTWs (1,100 kg/yr), from tributaries (3,800 kg/yr), and from diffusive fluxes (220 kg/yr) were developed and reported in the Source Characterization Report (URS Greiner Woodward Clyde 1998). These data are used in Figure 2-3, but on a dry/wet season basis. All flux calculations were performed in an Excel spreadsheet (Appendix B). The electronic spreadsheet is available upon request.

Also shown in Figure 2-3 are estimates of the net particulate flux exchange with the bed, and exchanges of dissolved and total water column fluxes between bay water at the Dumbarton Bridge. A range of estimates from these fluxes is provided, based on the choice of background station. Two alternative background stations were used: BB30 (where spatial concentration gradients of average concentrations tend to approach zero) and the average of BA30/BA40 (approximately one tidal excursion from the Dumbarton Bridge). A sensitivity analysis is also provided in Appendix B.

A parallel set of figures for nickel has been prepared: Figure 2-4 for the concentrations and Figure 2-5 for the inventories and loadings. The general approach to preparing the two sets of figures was the same. The following similarities and differences with respect to copper are noted:

- Like copper, the total average nickel concentration in the water column (23.8 µg/l) exceeds the average nickel concentration in the POTW discharge (5.1 µg/l), but by a larger amount

- The average surficial nickel concentration (99 to 109 mg/kg) is nearly the same as the background concentration (90 mg/kg) based on the deep core near the San Mateo Bridge, and is approximately equal to or less than the Tomales Bay deep core results (100 to 130 mg/kg).

- The mass of nickel above background in the top 1 meter of sediments (approximately 4.4 x 10^5 kg) is small compared to the total nickel mass there (3.2 x 10^6 kg to 5 x 10^6 kg).

The results presented in Figures 2-3 and 2-5 and in Appendix B show that the two largest sources of total copper and nickel to the Lower South San Francisco Bay are sediment exchange during resuspension and nonpoint source loads from tributaries. Most of the tributary loads occur during the wet season. Resuspension is highest during the windy spring and summer months, but also occurs during the rest of the year during periods of high winds or currents. During the dry season, the relative contributions of the POTW loads are higher than during the wet season since tributary nonpoint source loads become small.

Point sources are major contributors of dissolved copper and nickel, since nonpoint sources are believed to contribute primarily particulate loads. Internal cycling processes are also important components of the dissolved copper and nickel loads, particularly during the dry season. Mass balance calculations presented in Appendix B show that during the dry season, internal cycling fluxes occur that are similar in magnitude to the dissolved copper and nickel fluxes from the POTW discharges. These are the two largest sources of dissolved metals to the water column during this season. The specific processes causing the internal cycling fluxes cannot be identified with the available data, but they could include net desorption of metals during sediment resuspension, decomposition of algal detritus in the sediment, and solubilization of metals in phytoplankton during feeding by benthic bivalves. During the wet season, the mass balance calculations indicate that internal cycling processes result in a net sink of dissolved copper and nickel from the water. Again, the specific processes cannot be identified with the available data, but they could include net adsorption of metals on suspended solids entering the South Bay from tributary inflows and uptake by phytoplankton during the spring blooms. The magnitudes of the internal cycling fluxes are similar during both seasons, but they represent a dissolved source during the dry season and a dissolved sink during the wet season. The estimated cycling fluxes have high uncertainties due to the existing data limitations and simplifying assumptions required in the analyses.

Copper and nickel loads from sediment diffusion and atmospheric deposition appear to be relatively small, and together represent only a few percent of the total loads.

2.2 Conceptual Model for Copper

The conceptual model for copper is intended to be site-specific to Lower South San Francisco Bay. While many of the concepts are applicable to other systems, the relative importance of various processes and forcing functions are site-specific, as already illustrated in previous figures.

The environmental setting of San Francisco Bay, and surroundings, is shown in Figure 2-6 through Figure 2-9. The Sacramento and San Joaquin rivers that drain into San Francisco Bay comprise the San Francisco Bay watershed, which is approximately 63,000 square miles (mi^2) (Porterfield, 1980). Those rivers initially drain into the Delta region, where fresh and brackish waters meet, as illustrated in Figure 2-6. Also shown in Figure 2-6 are the various bays that comprise the greater San Francisco Bay, and include Suisun Bay, San Pablo Bay, Central Bay, and South San Francisco Bay. Lower South San Francisco Bay is that portion of the San Francisco Bay south of the Dumbarton Bridge. Figure 2-7 shows the Dumbarton Bridge and the portion of the Bay south of that bridge. The Lower South San Francisco Bay has a surface area of approximately 15 mi^2 (Beeman & Associates and Krone & Associates, 1992). The watershed that drains Lower South San Francisco Bay, shown in Figure 2-8, has a drainage area of approximately 800 mi^2 (Porterfield, 1980) and is only slightly smaller than the watershed that drains the remaining portion of South San Francisco Bay, also shown in Figure 2-8.

A three-dimensional rendition of the bathymetry of South San Francisco Bay and Lower South San Francisco Bay, based on data provided by Stanford University, is shown in Figure 2-9. A major feature of the bathymetry is the main channel that meanders through the Bay. Outside of this channel, Lower South San Francisco Bay is quite shallow, typically two meters or less. The channel in the Bay can be seen in its entirety in Figure 2-6, as depicted by the deeper blue color in the Bay. A distinct channel is present throughout both Central and San Pablo bays.

An overview of the conceptual model for copper is presented in Figure 2-10. Even though Lower South San Francisco Bay is relatively small, a much larger area must be considered in the conceptual model. This is because the fate of copper in Lower South San Francisco Bay is influenced by the tidal forcing that originates at the Golden Gate, where the Bay and the Pacific Ocean join. Tidal effects propagate into Lower South San Francisco Bay. Additionally, large volumes of freshwater periodically discharge into the Bay through the Delta from the Sacramento and San Joaquin Rivers, typically at discharge rates between 1,000 cubic meters per second (m^3/s) to 10,000 m^3/s. Some of this fresh water can propagate into South San Francisco Bay. As mentioned previously, these rivers drain a large area within California, particularly the wetter northern part of the state.

Even though the processes that occur within the watershed are significant with respect to the fate of copper and nickel, the conceptual model does not extend into the watershed. Rather, watershed processes are presumed to be quantitatively represented, and the conceptual model focuses on in-Bay processes.

Copper in the water column or in the bedded sediments can be present in different forms: particulate, dissolved, colloidal, within biota, or precipitated as a solid. In the water column, copper oxidizes from Cu(I) to Cu(II), and speciates into a variety of inorganic and organic complexes. Also in the water column, copper adsorbs to solid particles, and thereby provides the important linkage with the suspended and bedded sediments. Bioavailable forms of copper can be taken up by living organisms, both in the water column and in the bedded sediments.

In the bedded sediments, conditions that reduce Cu(II) to Cu(I) are more likely to be present than they are in the water column, particularly with increasing depth within the sediments. Copper reduction from Cu(II) to Cu(I) can mean that the concentration of dissolved copper will tend to decrease over depth within the sediments, even if the total concentration does not (which would include precipitated forms), since solubility of the reduced copper can limit the dissolved concentrations more than in an oxidized environment.

The cycling of copper is influenced by organisms in the water column and in the sediments. Phytoplankton and other organisms remove copper from the water through uptake processes. Copper is released to the water through decomposition and mineralization of phytoplankton and other organic debris, through excretion processes, and through solubilization of copper during feeding (e.g., benthic feeding on phytoplankton). Copper can accumulate in the food web, and at high enough concentrations can exert toxic effects on the organisms and their consumers. Accumulation of copper in the aquatic food web depends on uptake from two routes of exposure: water and food. For primary producers, such as phytoplankton, water is the source of uptake, while for aquatic animals both food and water are potentially important.

Implicit in the conceptual model for copper is a water budget. A water budget states that water entering Lower South San Francisco Bay must go somewhere (for example, mix with the saline water and flushed out of the system). Typically, where and how water enters and leaves the Lower South San Francisco Bay (and including storage within the Bay) needs to be known before the fate of copper can be evaluated with any degree of certainty. One reason for this is that sources of water are also sources of copper, and losses of water usually represent losses of copper. There are several exceptions, however. Copper can enter the Bay from dry particulate deposition. Also, water can evaporate into the atmosphere from the surface of the Bay, while the copper remains behind.

2.3 Conceptual Model for Nickel

The conceptual model for nickel is shown in Figure 2-11. Great similarities exist between the conceptual models for nickel and for copper, as can be seen by comparing Figure 2-11 with Figure 2-10. For example, the same source types exist for nickel as for copper, although the concentrations and magnitudes of loadings differ, as shown previously in Figures 2-3 and 2-5. In the Lower South San Francisco Bay itself, copper and nickel cycling and transport processes are similar. One major exception is that nickel is expected to be present in the Ni(II) oxidation state, whether in the water column or sediment, where as copper can be present in both Cu(I) and Cu(II) oxidation states. As a result of these similarities, a strong correlation exists between copper and nickel concentrations in the water column in South San Francisco Bay. This correlation is discussed in Section 6. In general, however, less is known about the specifics of nickel cycling (such as rates of adsorption and desorption) compared with copper cycling.

2.4 Summary

1. The largest source of total copper presently appears to be from net exchange of particulates from the bed into the water column. Desorption rates into the dissolved phase exceeds adsorption rates back to the adsorbed phase for the dry season only. The second largest source of total copper (on an annual basis) is from nonpoint sources. For nickel, the net exchange of particlulates with the water column is the second largest source (nonpoint sources are larger).

2. On an annual basis, point sources are the third largest contribution of the total loads of copper and nickel to Lower South San Francisco Bay. However, point sources are major contributors of dissolved copper and nickel, since nonpoint sources are believed to contribute primarily particulate loads.

3. Internal cycling processes are also important components of the dissolved copper and nickel loads, particularly during the dry season. During the dry season, internal cycling fluxes are similar in magnitude to the dissolved copper and nickel fluxes from the POTW discharges. During the wet season, internal cycling processes result in a net sink of dissolved copper and nickel from the water. The specific processes causing the internal cycling fluxes cannot be identified with the available data. Potential sources could include net desorption of metals during sediment resuspension, decomposition of algal detritus in the sediment, and solubilization of metals in phytoplankton during feeding by benthic bivalves. Potential sinks could include net adsorption of metals on suspended solids entering the South Bay from tributary inflows and uptake by phytoplankton during the spring blooms.

4. Loadings from the atmosphere and from diffusive sediment fluxes, although subject to large uncertainties, appear to be one to two orders of magnitude less than loadings from other sources.

5. Residence time of conservative solutes in Lower South Bay is approximately 20 days during the dry season (Appendix A; Gross (1997))

6. Point source discharges appear to contribute no more than 0.5 µg/l of copper and 1.0 µg/l of nickel to the water column (averaged over the Lower South Bay) during the dry season (see Appendix B).

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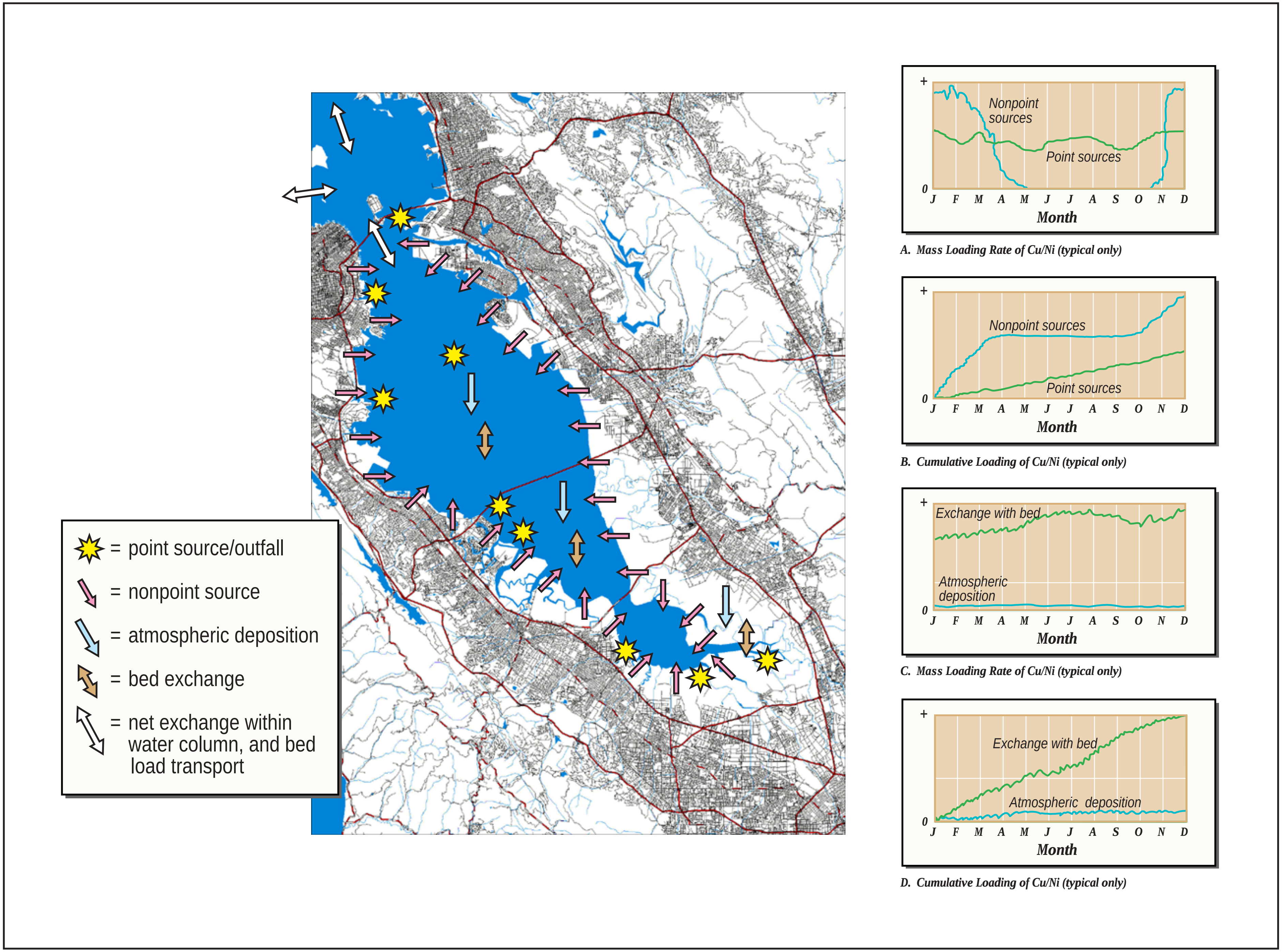


Figure 2-1. Conceptual model of copper and nickel loading to South San Francisco Bay.

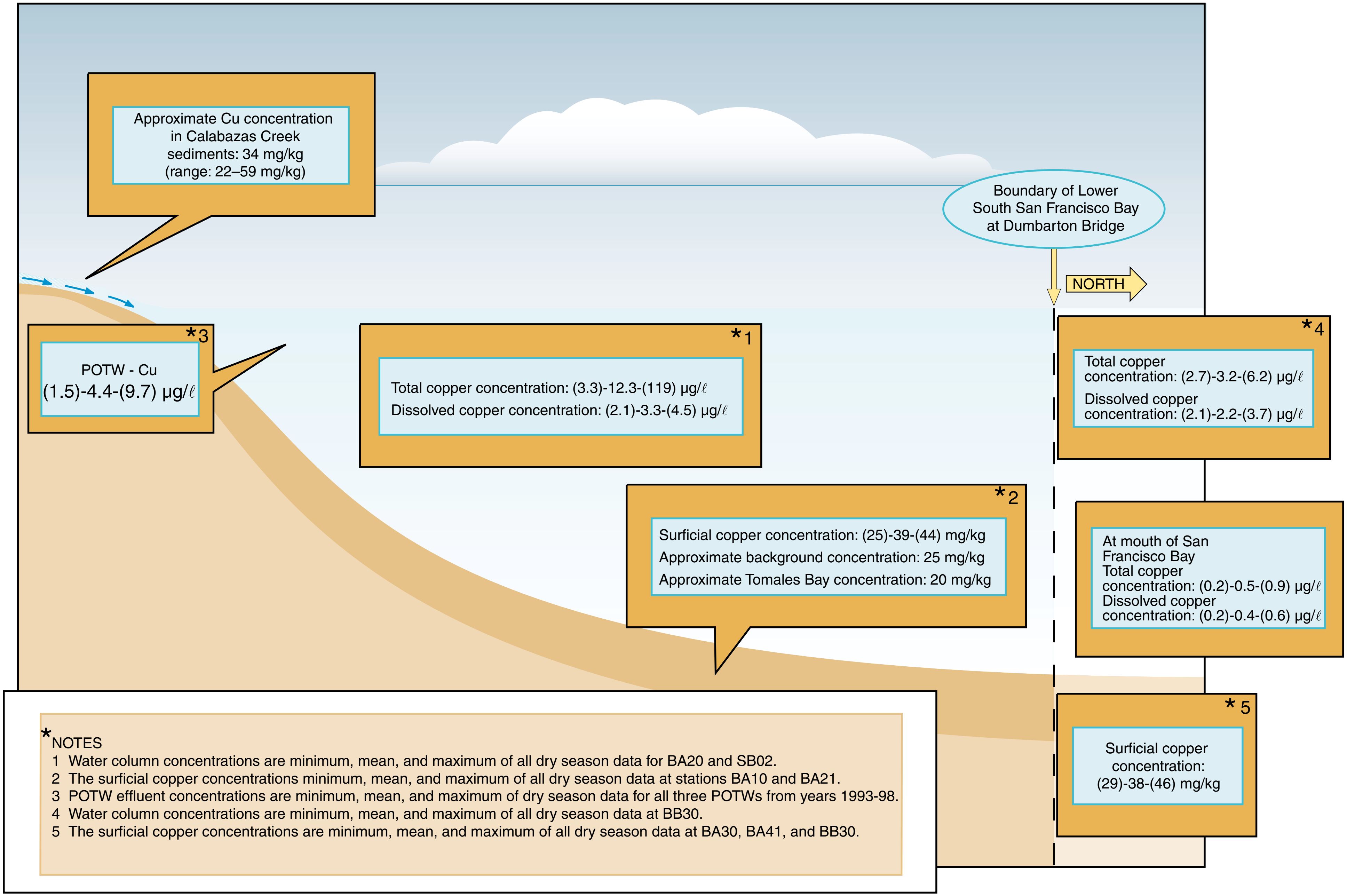


Figure 2-2a. Copper concentrations in Lower South San Francisco Bay during dry season.

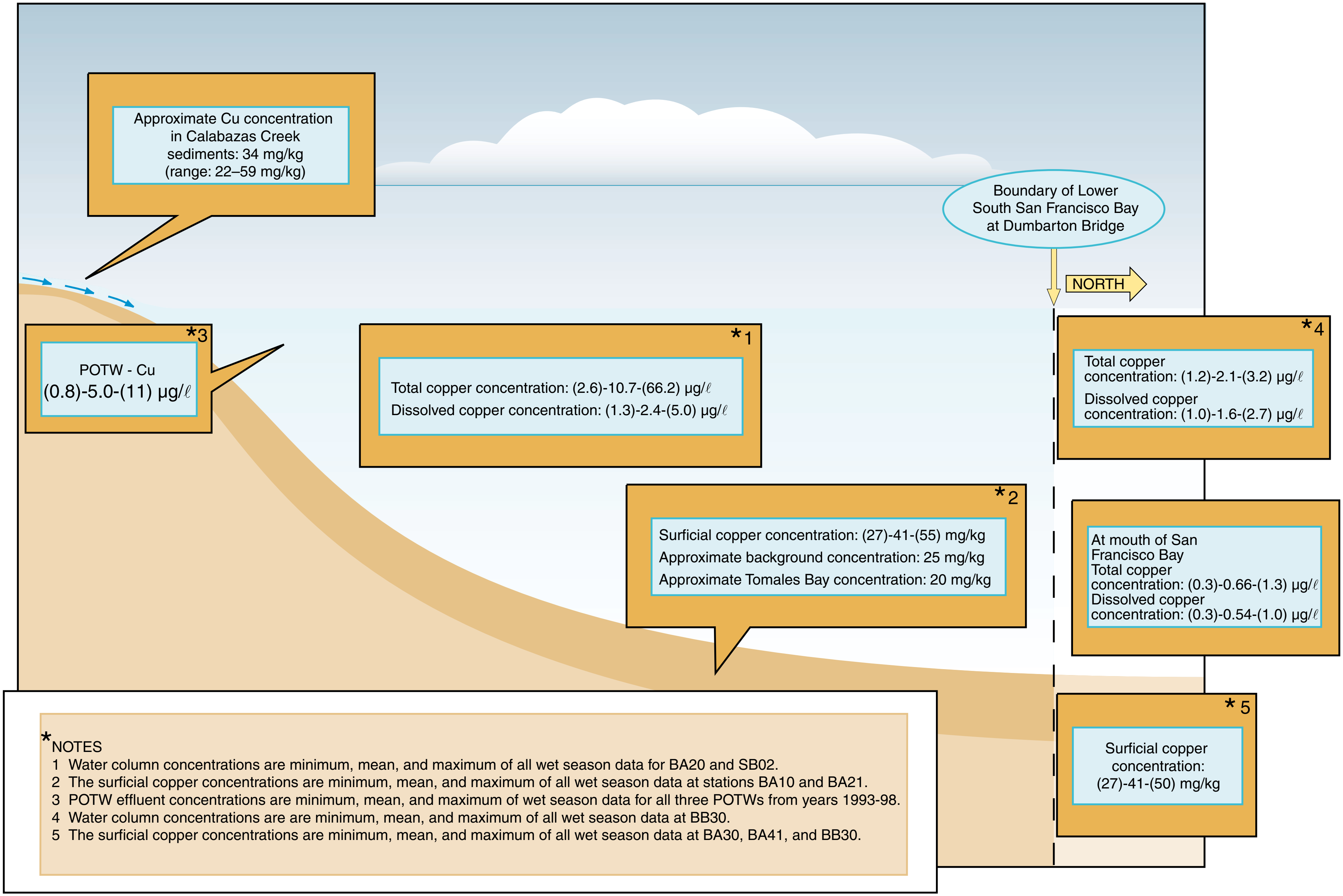


Figure 2-2b. Copper concentrations in Lower South San Francisco Bay during wet season.

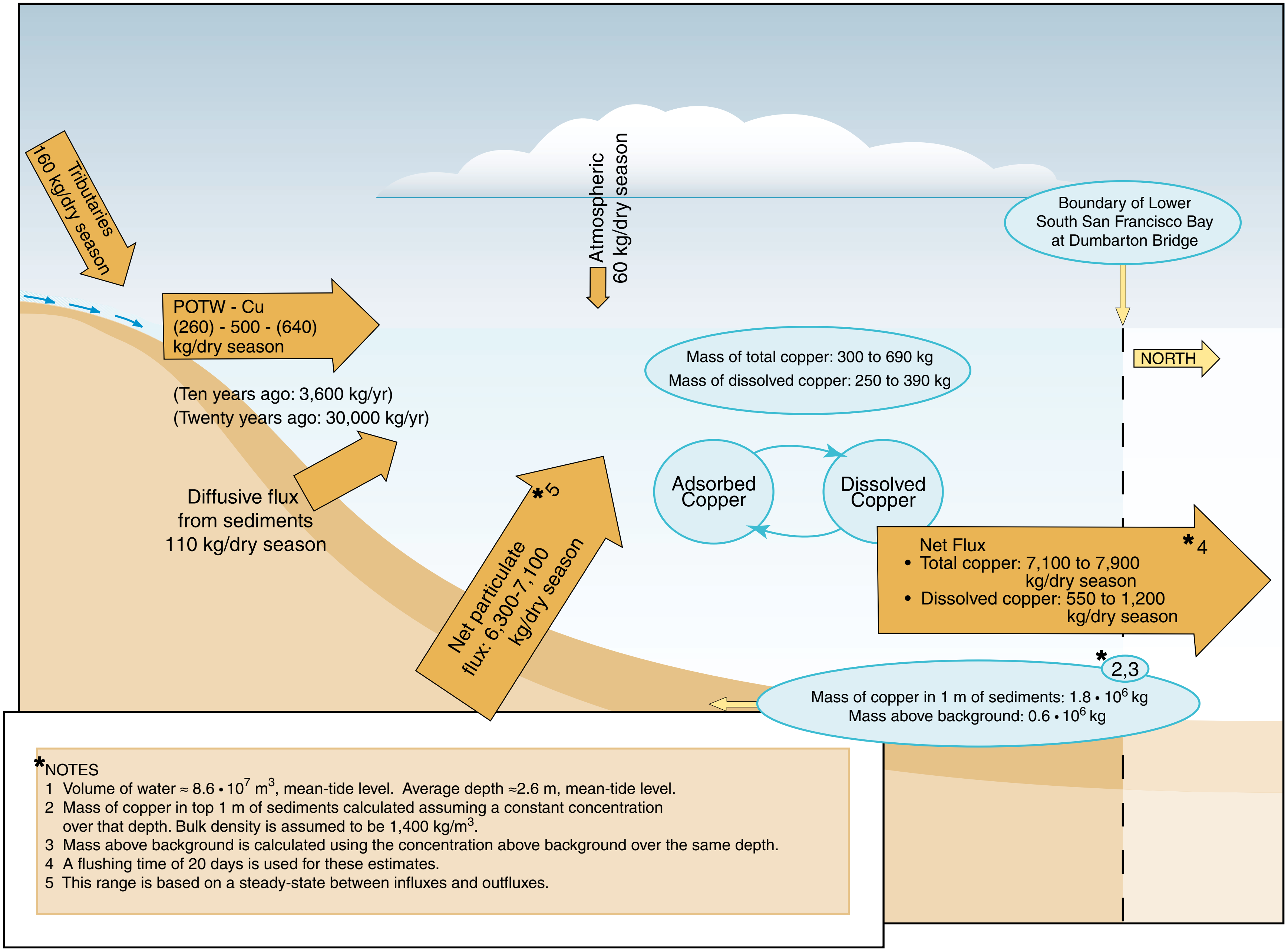
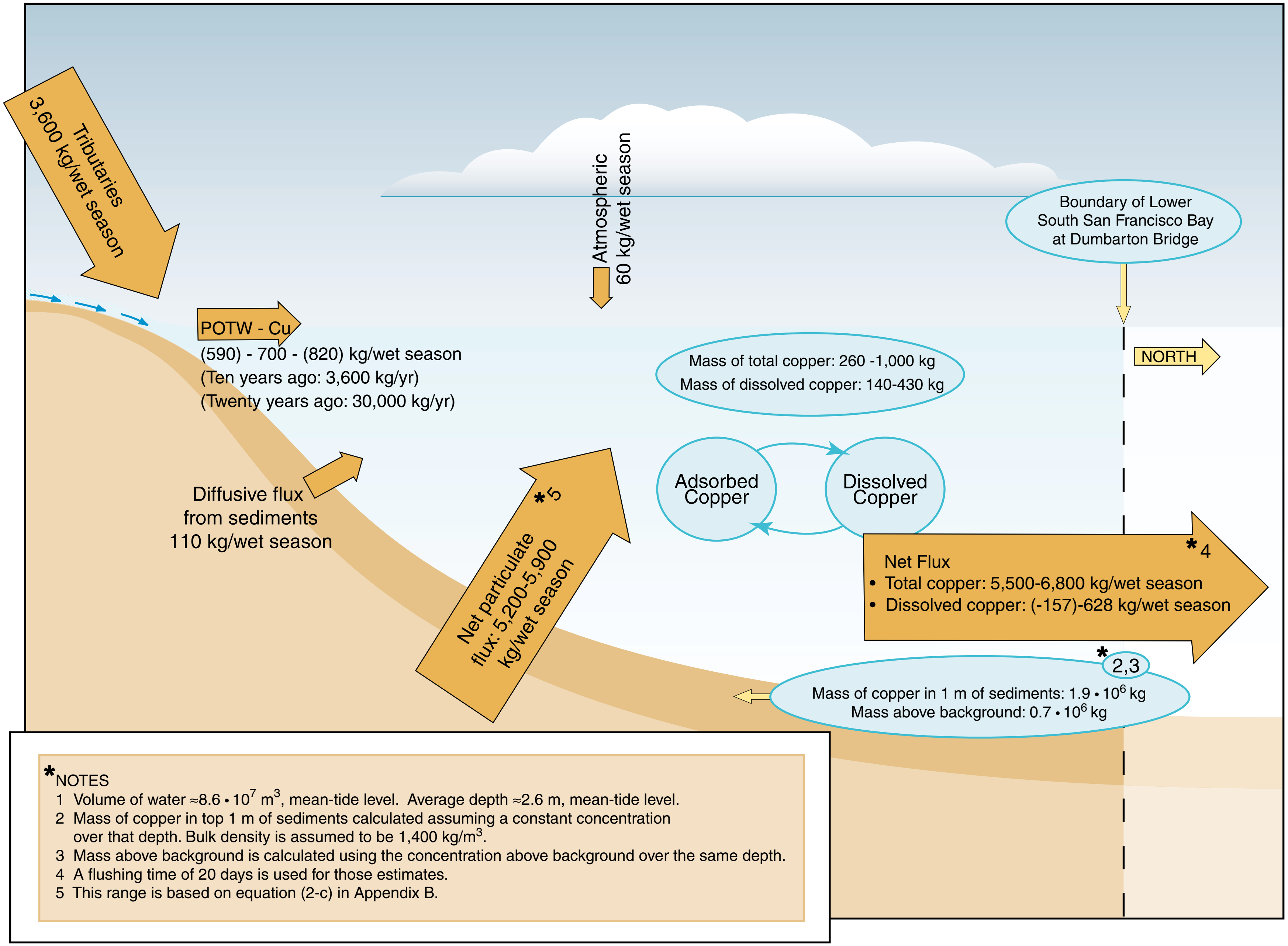


Figure 2-3a. Copper inventories and loadings in Lower South San Francisco Bay during the dry season.



*NOTES

1 Volume of water ≈8.6 • 10^7 m^3, mean-tide level. Average depth ≈2.6 m, mean-tide level.
2 Mass of copper in top 1 m of sediments calculated assuming a constant concentration over that depth. Bulk density is assumed to be 1,400 kg/m^3.
3 Mass above background is calculated using the concentration above background over the same depth.
4 A flushing time of 20 days is used for those estimates.
5 This range is based on equation (2-c) in Appendix B.

Figure 2-3b. Copper inventories and loadings in Lower South San Francisco Bay during the wet season.

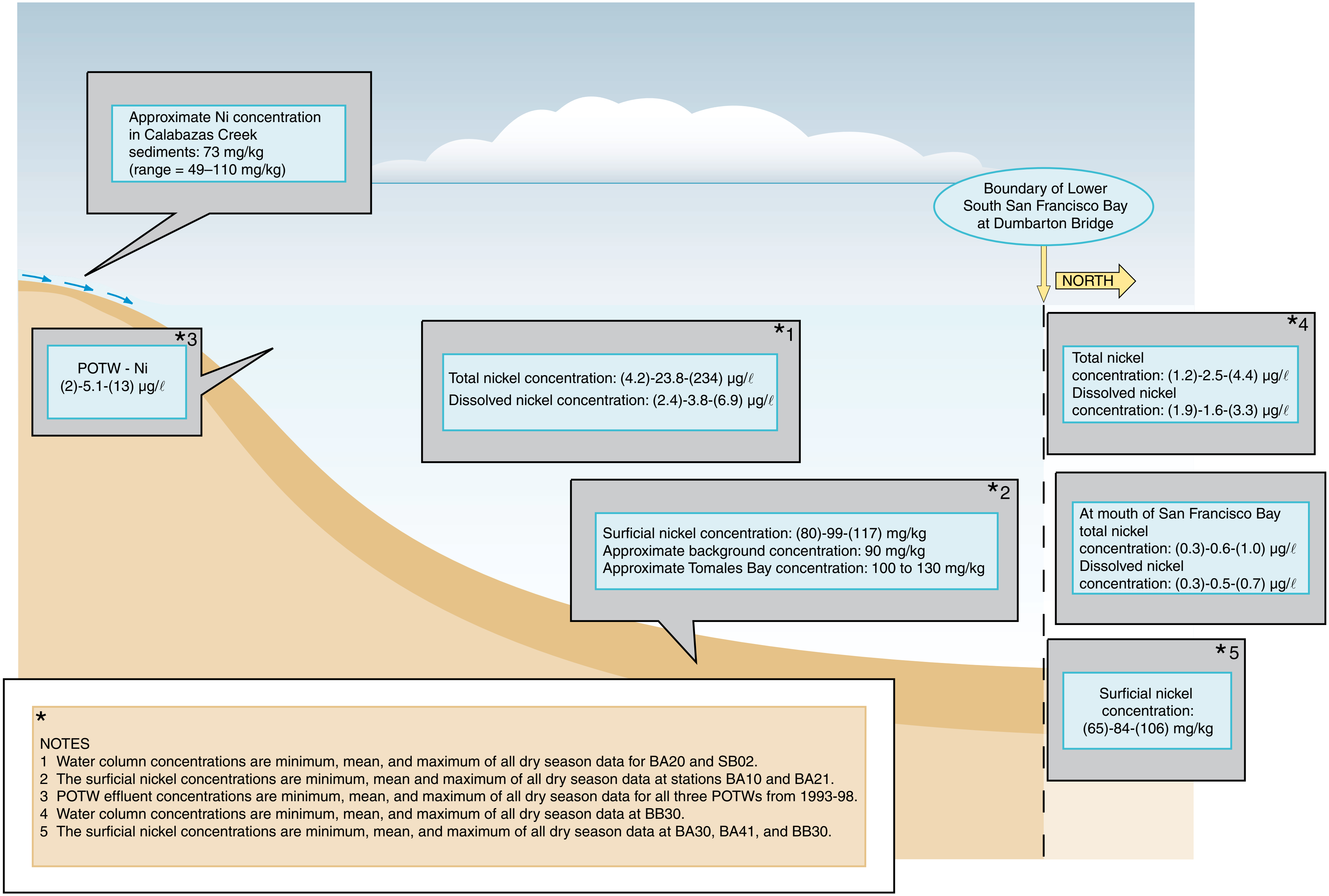


Figure 2-4a. Nickel concentrations in Lower South San Francisco Bay during dry season.

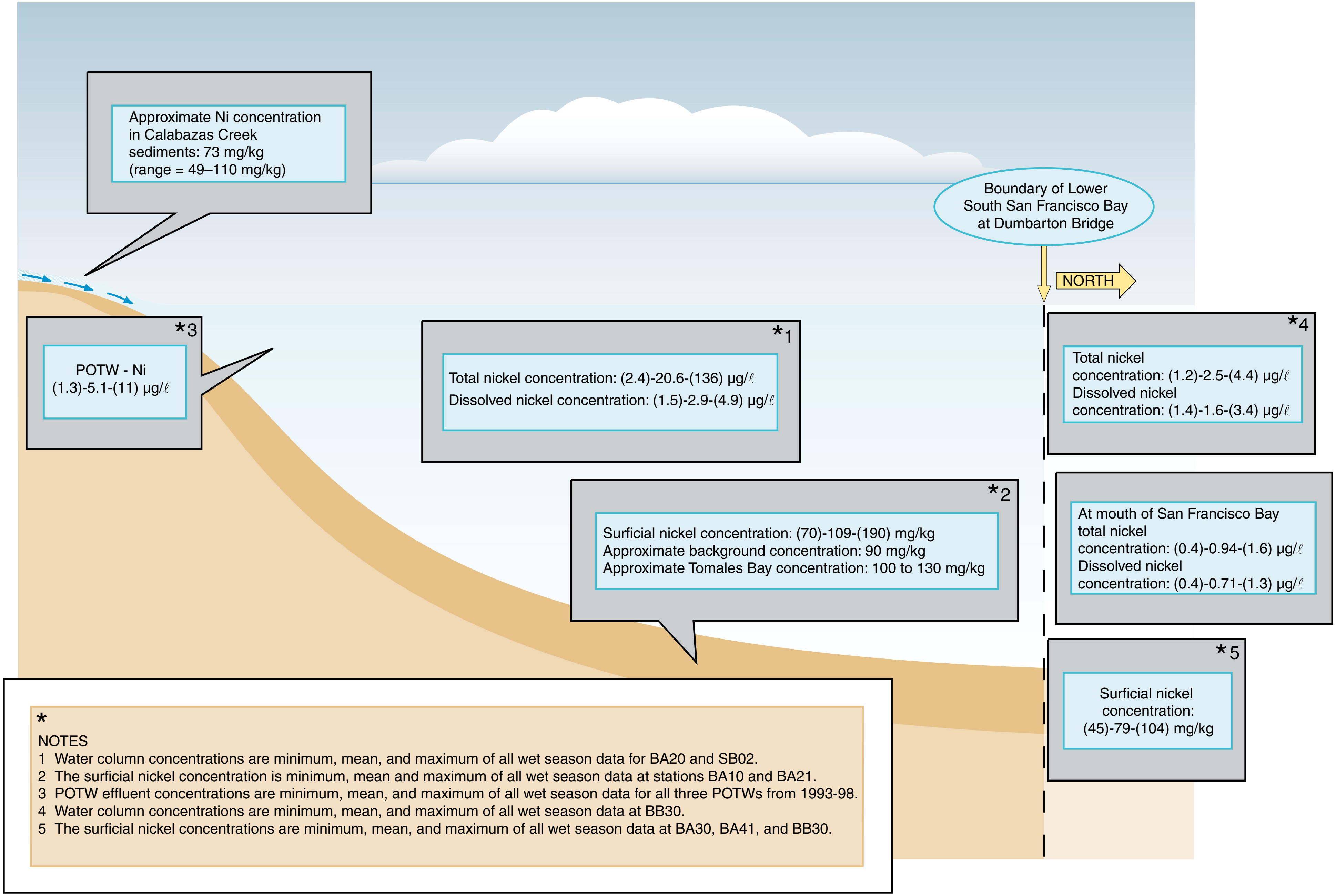
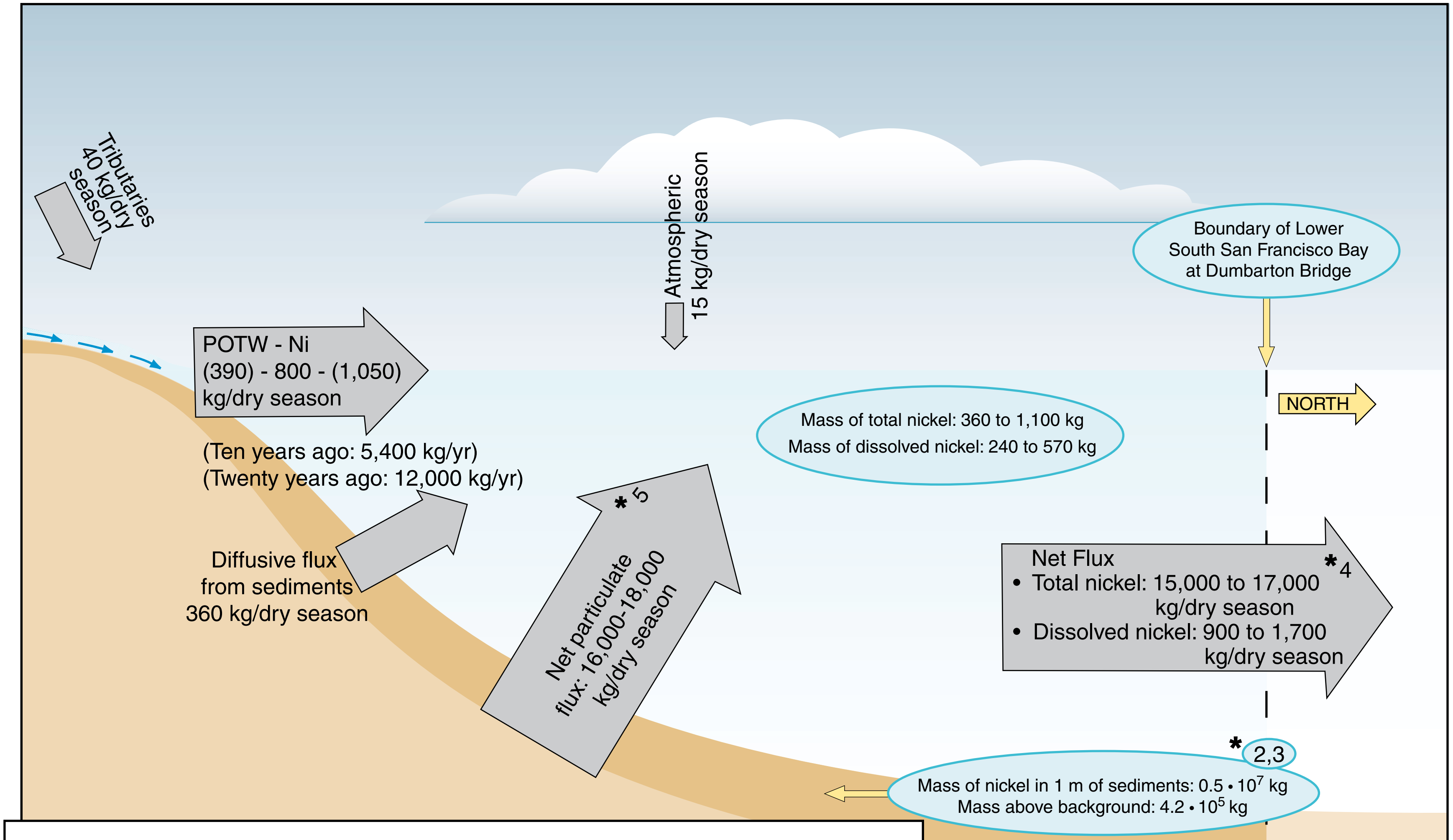


Figure 2-4b. Nickel concentrations in Lower South San Francisco Bay during wet season.



*NOTES

1 Volume of water ≈8.6 • 10^7 m^3, mean-tide level. Average depth ≈2.6 m, mean-tide level.
2 Mass of nickel in top 1 m of sediments calculated assuming a constant concentration over that depth. Bulk density is assumed to be 1,400 kg/m^3.
3 Mass above background is calculated using the concentration above background over the same depth.
4 Estimates are based on flushing time= 20 days.
5 The estimates are based on Equation (2-b) in Appendix B.

Figure 2-5a. Nickel inventories and loadings in Lower South San Francisco Bay during dry season.

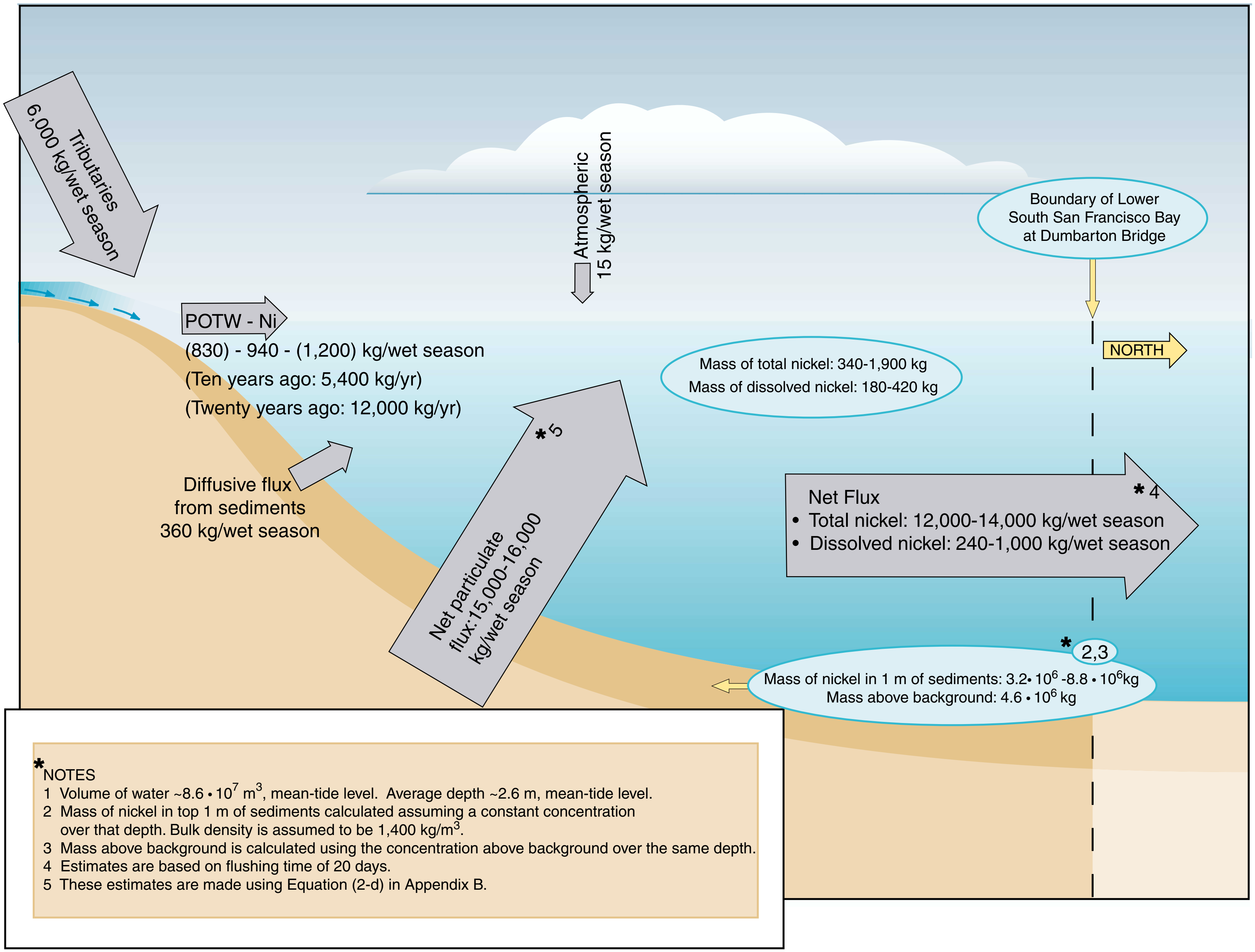


Figure 2-5b. Nickel inventories and loadings in Lower South San Francisco Bay during wet season.

Figure 2-6. San Francisco Bay and Delta Region.

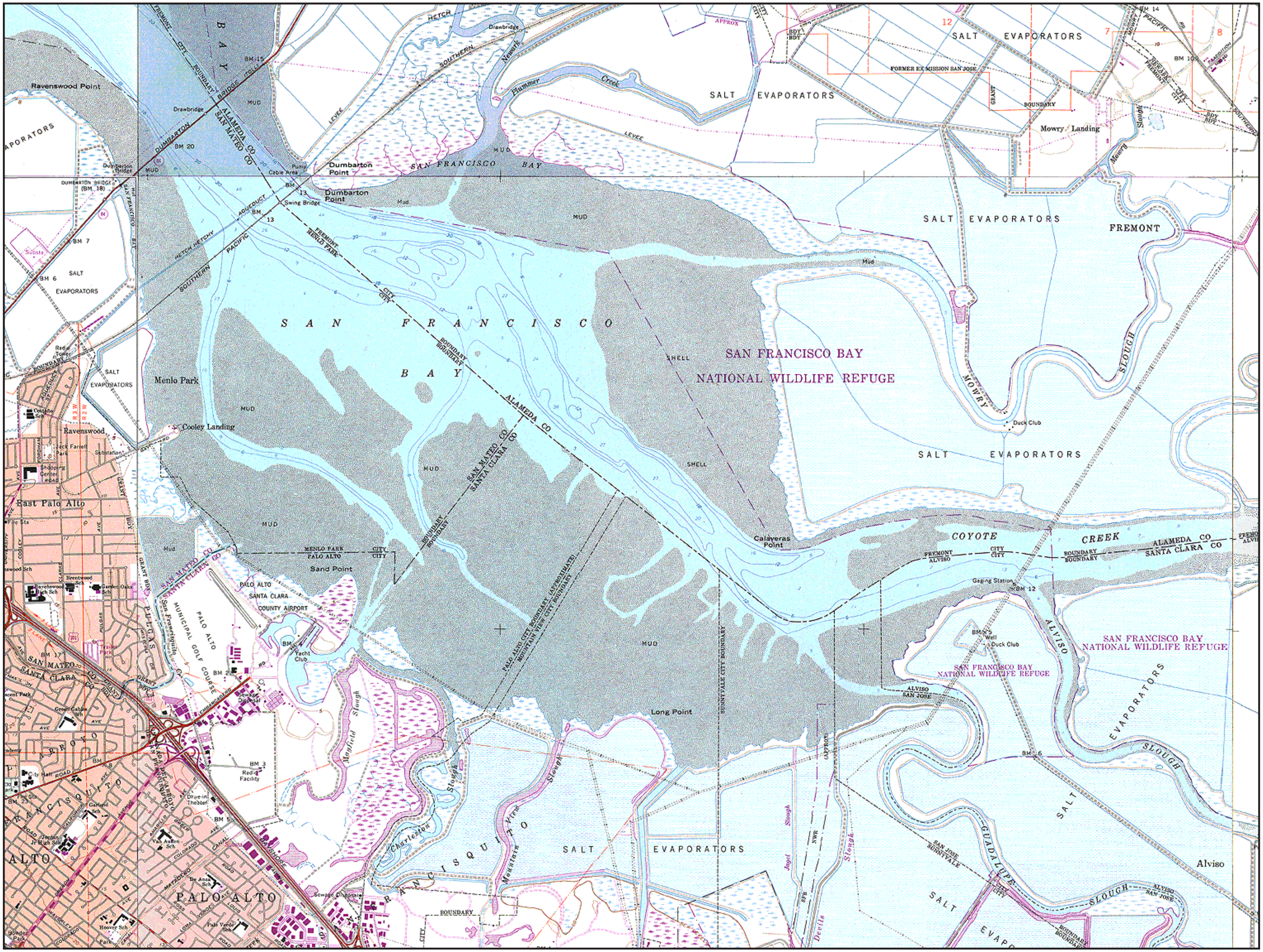


Figure 2-7. Lower South San Francisco Bay and environs.

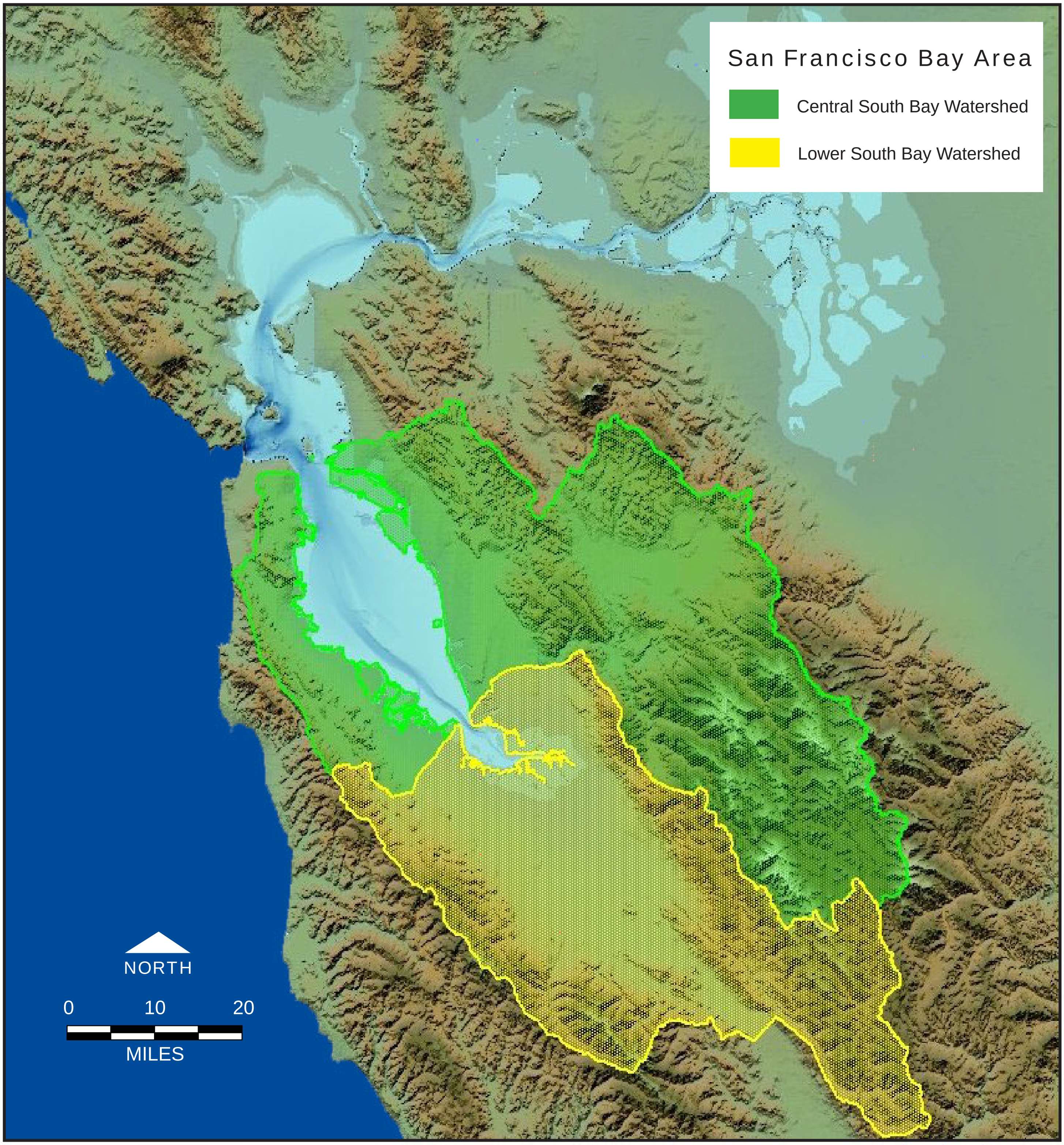


Figure 2-8. San Francisco Bay and South Bay Watersheds.

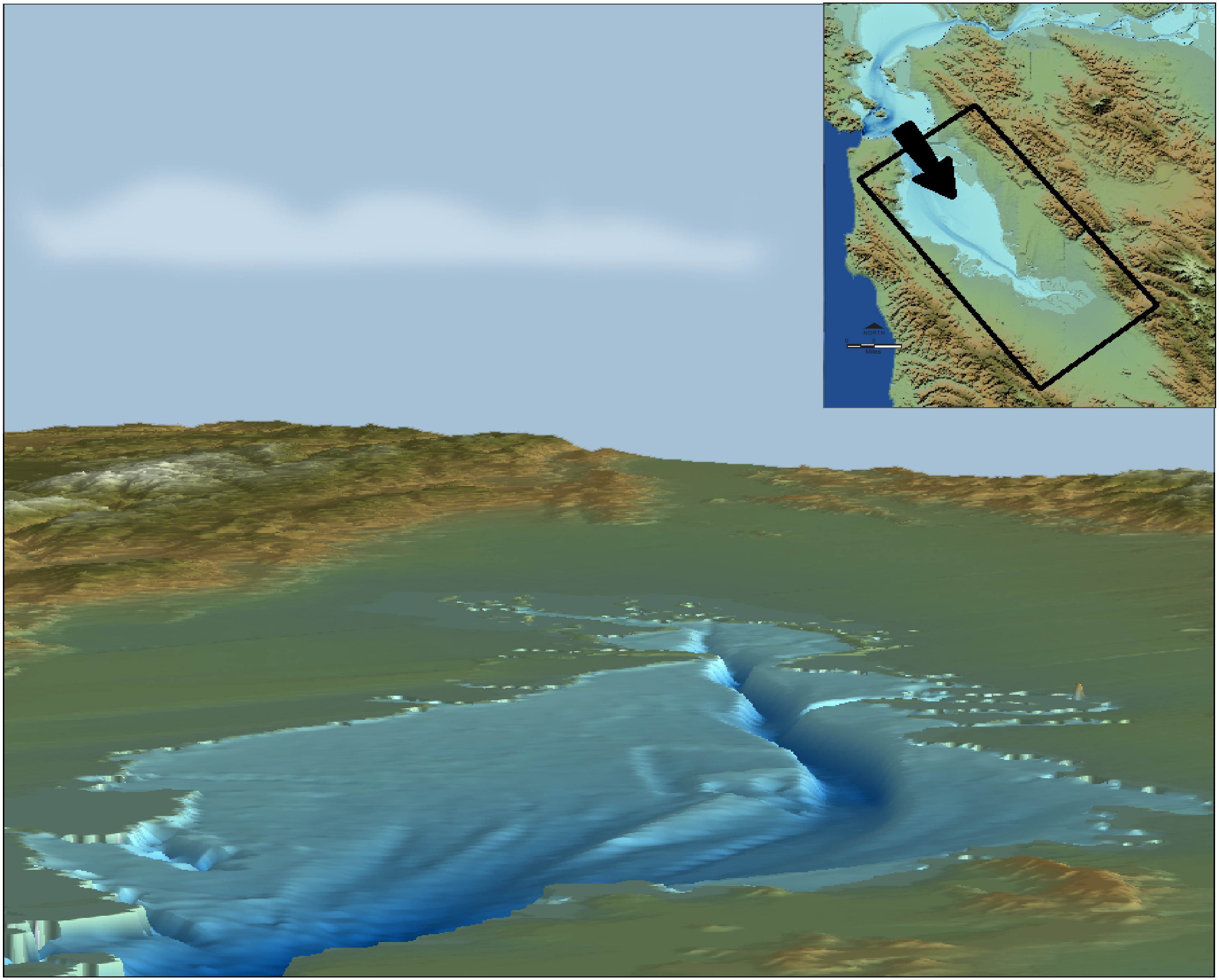


Figure 2-9. Three-dimensional bathymetric map of South San Francisco Bay, at 50 times exaggeration.

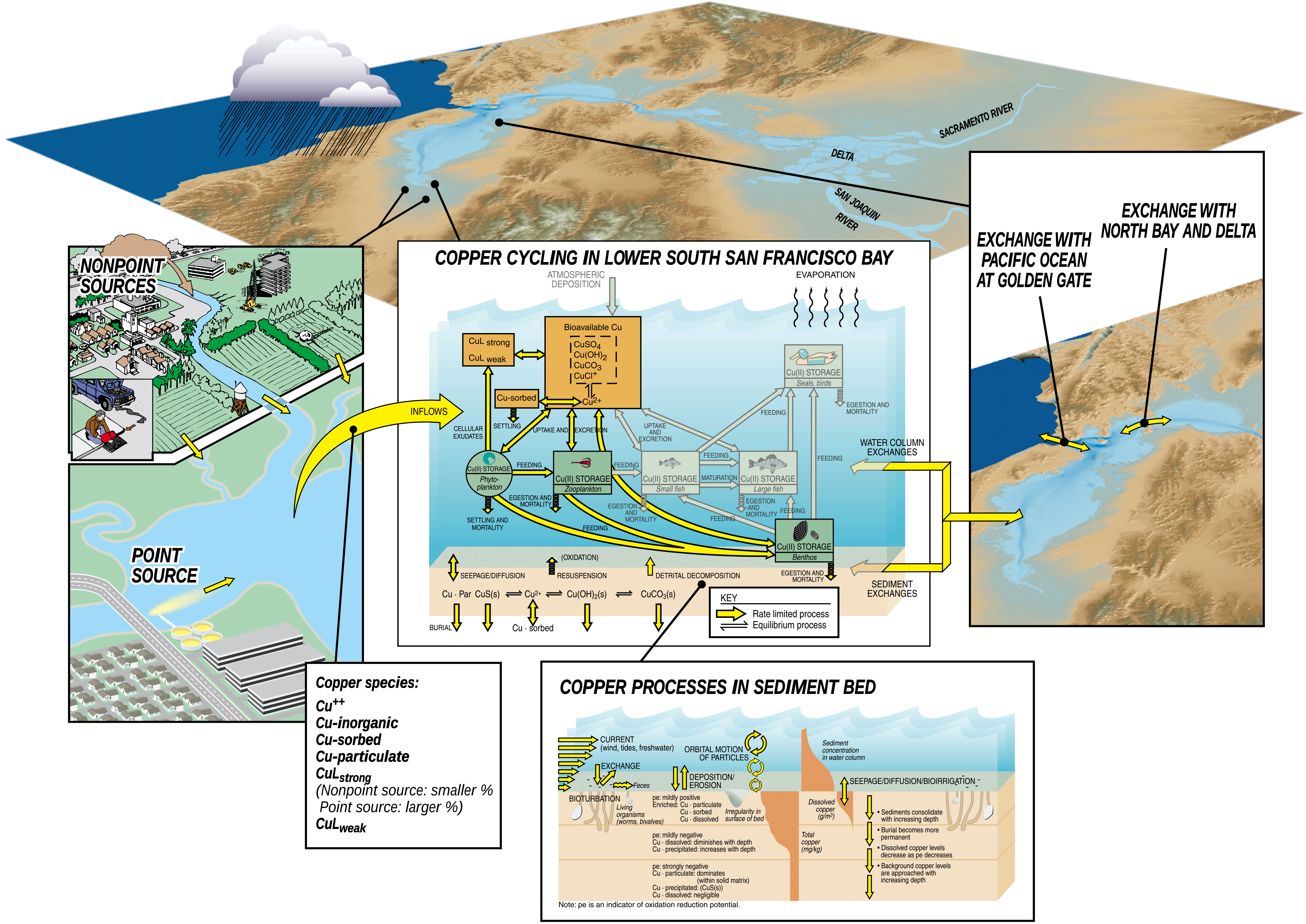


Figure 2-10. Conceptual model of copper for Lower South San Francisco Bay.

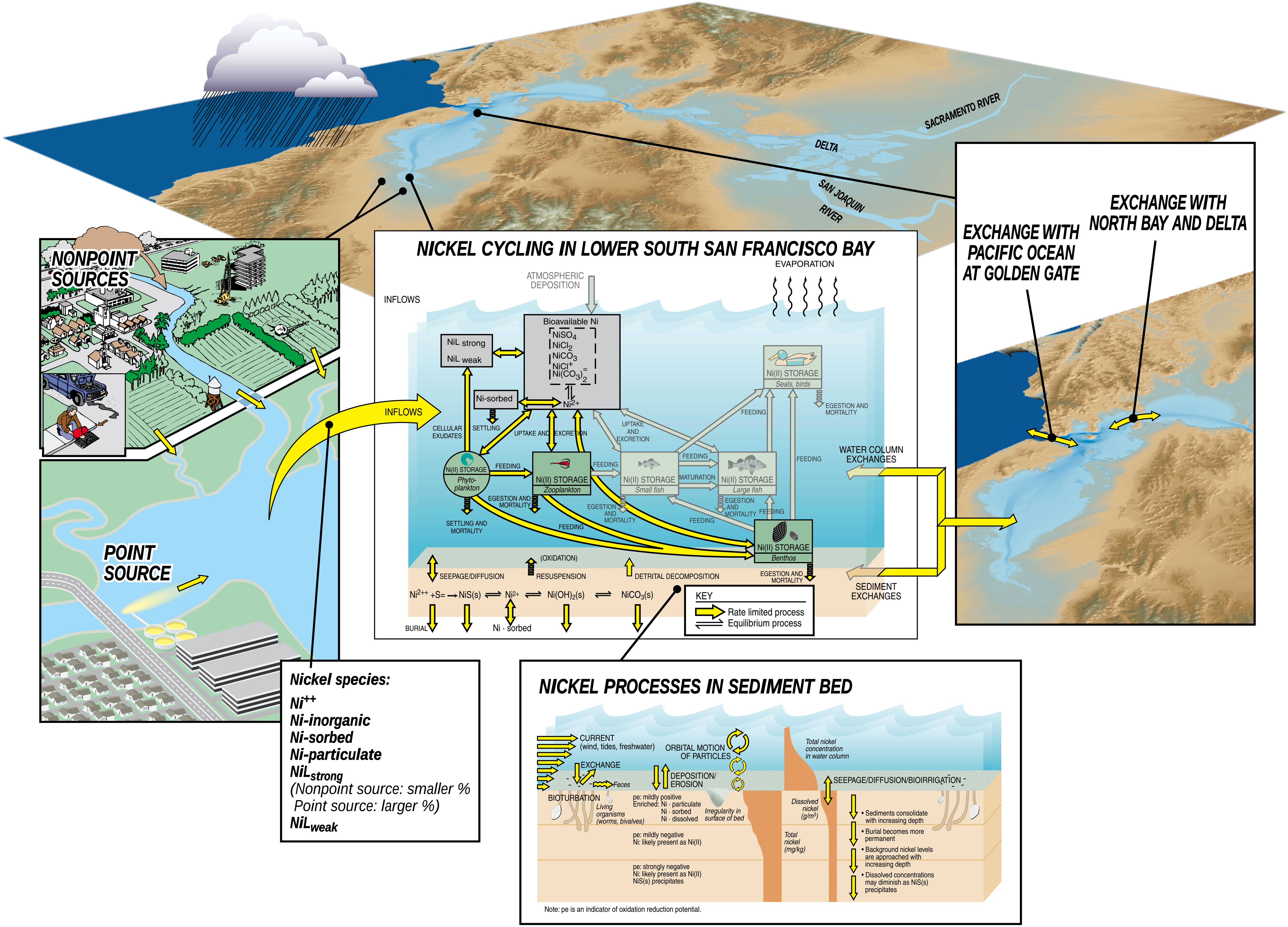


Figure 2-11. Conceptual model of nickel for lower South San Francisco Bay.

3 CONCEPTUAL MODEL OF SEDIMENT TRANSPORT

3.1 Description

The transport of sediment into, within, and out of Lower South San Francisco Bay is an important component of the copper and nickel cycling process because both copper and nickel are adsorbed to the surfaces of, or embedded within the matrix of, solid particles. Large net loading of copper and nickel into the water column are thought to originate as particulates from the bed and then a net desorption occurs that acts as an internal source of dissolved copper, as discussed in Section 2 (estimates for nickel were not discussed). The overall process of sediment cycling is referred to as the sediment budget. The conceptual model of the sediment budget for Lower South San Francisco Bay is shown in Figure 3-1. The sources of sediments are shown in that figure and include:

- Runoff, including erosion, from urban and nonurban sources within the watershed, as shown in the upper left-hand portion of Figure 3-1. These loads are highly variable from year to year, and from the dry season to the wet season, as illustrated by the conceptual sediment loading rate inset to Figure 3-1. During the dry season, the natural streams may either dry up or discharge a minimal amount of sediment. Practically no sediments are transported in those streams during low-flow conditions due to lower stream flow velocities and low stream energy available to transport the sediments. However, over a time period of years, the nonpoint sources of sediments contribute more sediments than do the point sources.

- Three major point sources. In contrast to the large seasonal and yearly variability of loadings from nonpoint sources, point source loadings are more constant temporally. Over a long period of time, point source loadings of solids are small compared to nonpoint source loadings. During the dry season, point source loadings can exceed nonpoint source loadings.

- Exchange of suspended solids with Bay waters from outside of the study area, as well as exchange with bedded sediments through bed load transport.

- In situ particle generation (e.g., growth of phytoplankton) and particle depletion (e.g., consumption or death and decay of phytoplankton).

- Erosion from and deposition to the sediment bed.

As indicated previously, nonpoint source loads dominate the external sources of loading. Even so, loading estimates made to date, and reported by URS Greiner Woodward Clyde (1998b), have not considered the contribution of the entire watershed to Lower South San Francisco Bay. The subwatersheds where loading estimates have been made are shown in Figure 3-2. Note that the boundaries of the subwatersheds do not include the portions of the watersheds directly adjacent to Lower South San Francisco Bay itself. Thus, some net deposition of sediment loads can and does occur in these low gradient areas.

Solids that enter Lower South San Francisco Bay from freshwater inflows are subject to flocculation, since the salinity of the Bay is typically high enough to destabilize the solid particles (salinities typically range from 5 to 35 psu). Once in the Bay, the solids are subjected to gravitational forces and depositional shear stresses that tend to cause them to settle to the bed, as well as hydrodynamic forces such as erosional shear stresses that tend to keep the solids suspended (McDonald and Cheng, 1996). Typically, the concentration profile of suspended solids with respect to depth is not uniform, and concentrations increase with depth, as shown in Figure 3-1. Also, this is illustrated using a short time-series of suspended solids data collected at two different depths near the Dumbarton Bridge: mid-depth and near-bottom. Those data have been plotted, and are shown in Figure 3-3. While the two time series shown in that figure exhibit highly variable concentrations, it is clear that concentrations of suspended solids nearer the bed are likely to be higher than those located at mid-depth in the water column.

Within the water column, the solids are likely to consist primarily of the smaller clay-sized particles. In the bed, larger-sized particles are likely to be present, as well as smaller-sized particles. A conceptualization of the particle size distributions is included in Figure 3-1. Particle size distributions are likely to vary temporally, from season to season, as the sources of those particles (and the forcing functions that influence their fate) change (Thompson-Becker and Luoma, 1985).

A summary of the major forcing functions and relevant processes is shown in Figure 3-4. On the left part of the figure, the temporal scales are those scales associated with the duration of the phenomenon, such as the seasonal scales of loadings from the watershed (months or seasons), or the instantaneous wind velocities (minutes to hours). Because of the many processes and the time scales associated with their manifestation, the accurate quantification of sediment resuspension, transport, and deposition is difficult (McDonald and Cheng, 1996). On the right-hand side of the figure, the forcing functions of wind speeds and the spring-neap tidal cycles are shown. The current speeds that are generated from winds and tides are also shown.

In Lower South San Francisco Bay, water depth is both spatially and temporally variable. Figure 3-5 illustrates three cross sections (A, B, and C) and one longitudinal section (D) in Lower South San Francisco Bay. The bathymetric data used to develop these sections was provided by Stanford University, and is discussed by Gross (1997). A deep channel is present in Lower South San Francisco Bay at Section A, near the Dumbarton Bridge (its approximate depth is 15 meters), and that deep channel gradually diminishes in depth from Section A to Section C (where it is no more than a few meters in depth). As this occurs, a larger portion of the Bay becomes very shallow. One significant effect of this configuration is that the tidally generated currents and wind-generated currents manifest themselves differently between the shoal and channel areas. A portion of Figure 3-4 illustrates this, by showing how velocity profiles can differ between the shoals and channels for the two forcing functions. In the channels, tidally generated currents are likely to exert larger shear forces on the bed, while in the shoals, the opposite is likely to be true: wind-generated waves and currents are likely to be responsible for the larger shear forces to induce particle resuspension (Lacy, et al., 1996).

A second significant effect of the bathymetric configuration of Lower South San Francisco Bay is that drying and wetting of a significant portion of the sediment bed is associated with tidally induced water surface elevation changes. This is illustrated in Figure 3-3. That figure shows the approximate range between higher high water and lower low water at a location near the Dumbarton Bridge. Note that at lower low water much of the bedded sediments are exposed to the atmosphere, and then rewetted again as the tide rises. Thus the forces that influence sediment resuspension and deposition are temporally and spatially variable.

3.2 Summary

1. Sediment transport is important to the cycling of both copper and nickel, and sediments resupended from the bed appear to be an important internal copper and nickel source.

2. A fraction of sediments that erode from the watershed appear to be deposited in streambeds in the flatlands, and may enter the bay during subsequent storm events.

3. A size differential likely exists between suspended particulates and sediments in the bed, and would have implications on the fate of copper and nickel (metals likely associate more strongly with the smaller particles).

4. Wetting and drying of the sediment bed is a prominent feature of the Lower South Bay that influences sediment transport.

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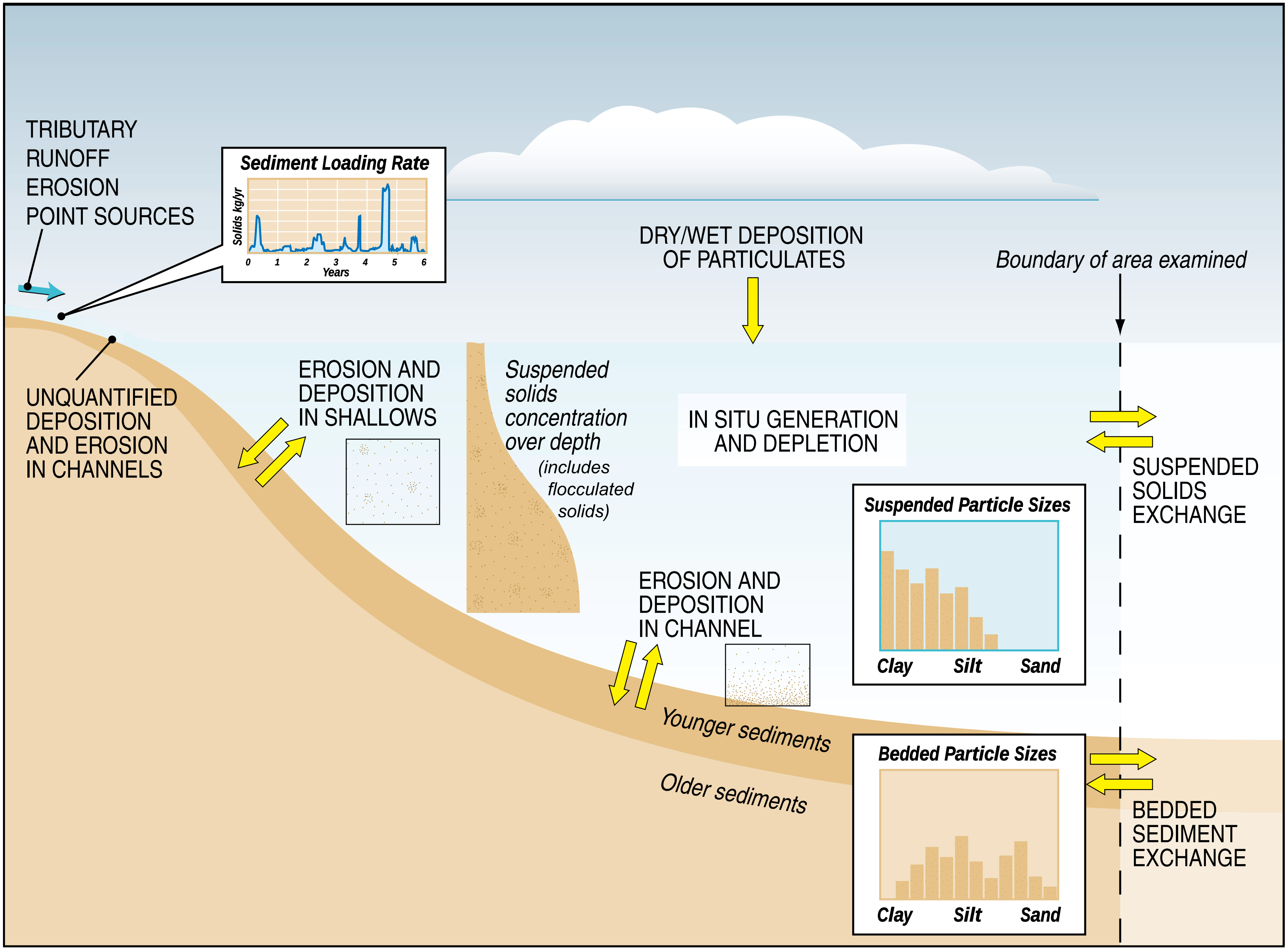

Figure 3-1. Major components of sediment budget for Lower South San Francisco Bay.

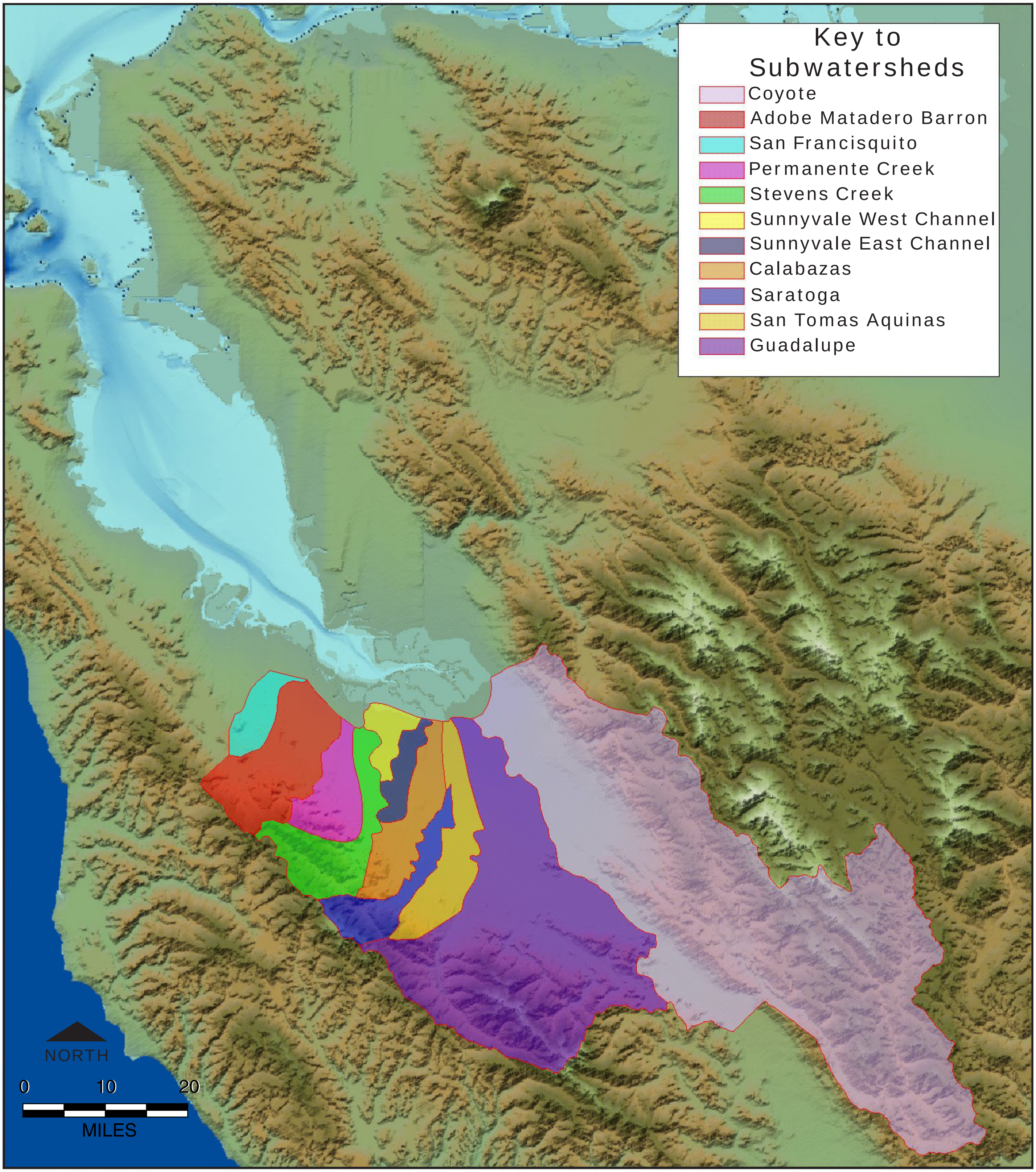

Figure 3-2. Lower South San Francisco Bay Subwatersheds used for loading assessment studies.

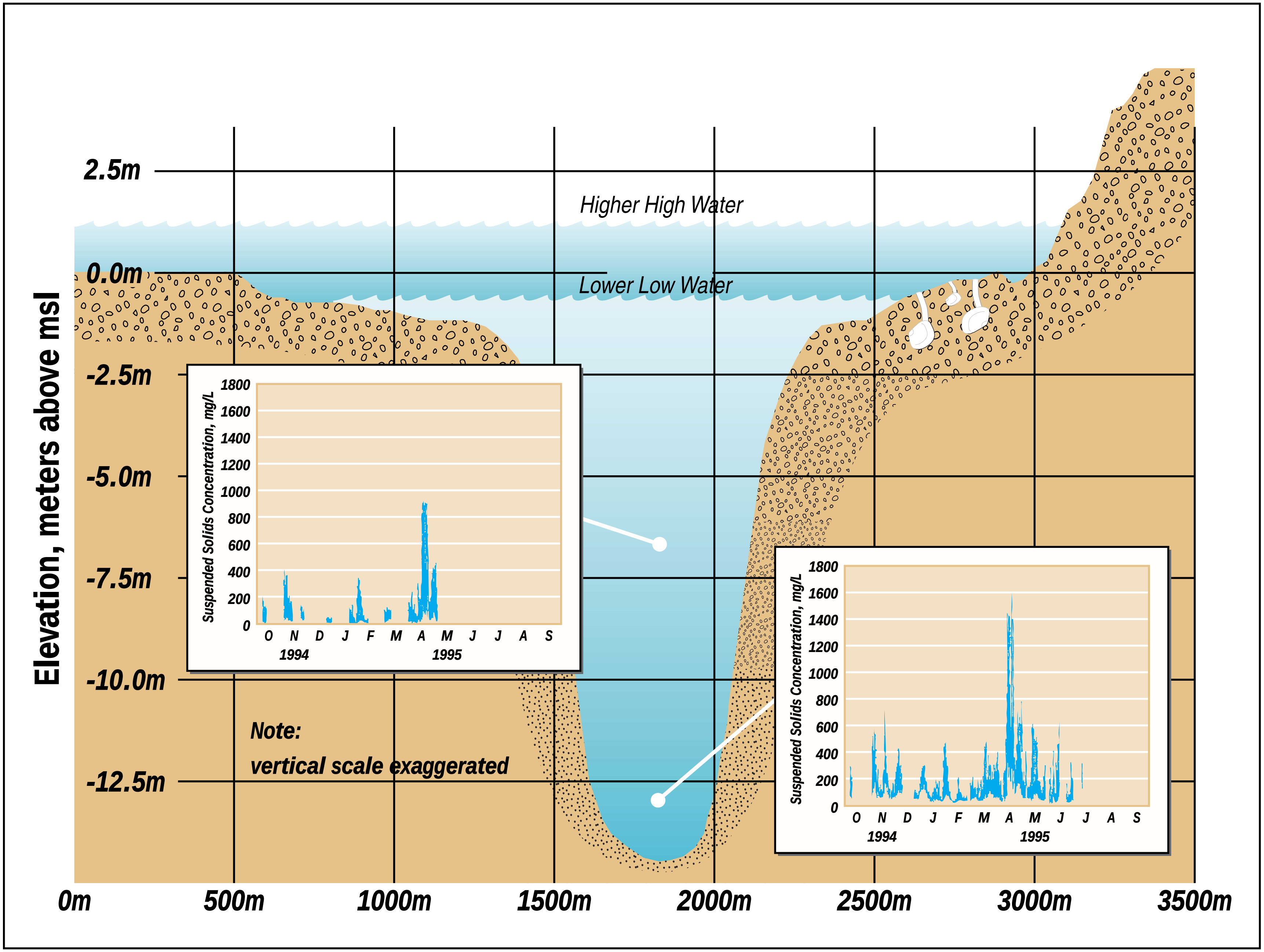

Figure 3-3. Illustration of increased sediment concentrations near the bed as compared to higher in the water column, using a cross section of Lower South San Francisco Bay at the Dumbarton Bridge.

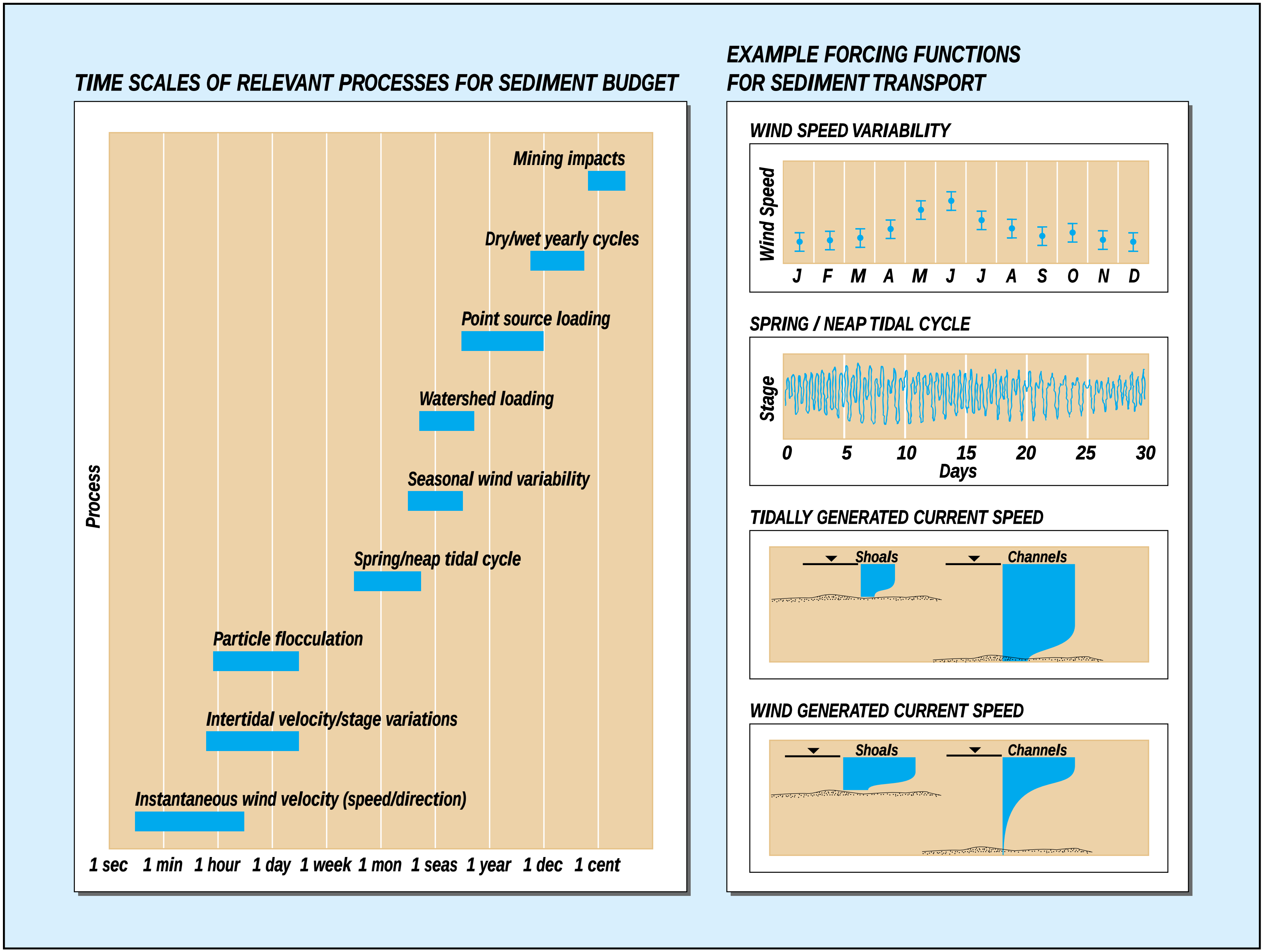

Figure 3-4. Relevant time scales and forcing functions associated with sediment transport.

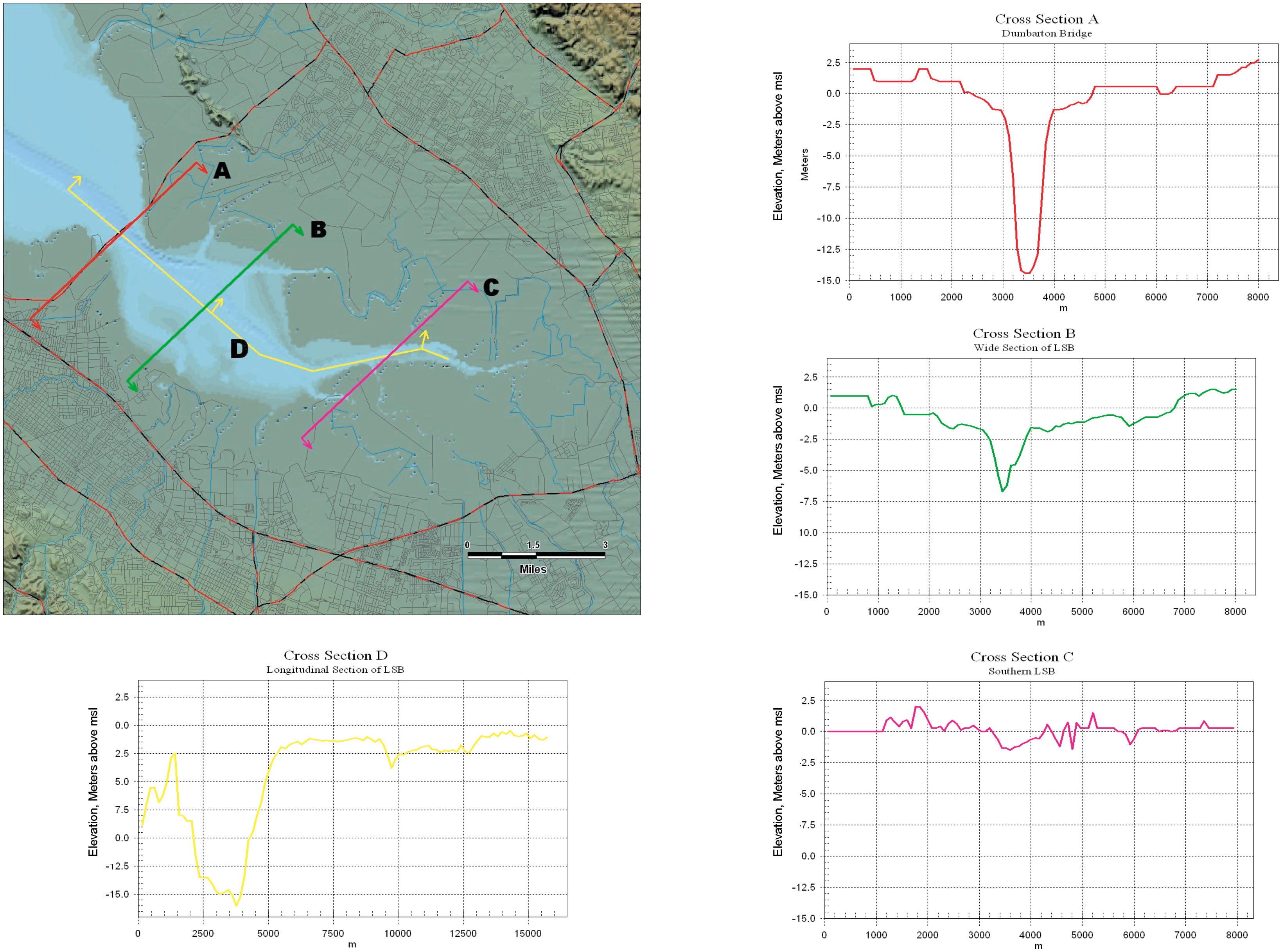

Figure 3-5. Three cross sections of Lower San Francisco Bay and one longitudinal section through Lower South San Francisco Bay